

# RUBBER CHEMISTRY AND TECHNOLOGY

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## RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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# THE VARIATION WITH TEMPERATURE OF THE DYNAMIC PROPERTIES OF RUBBER AND SYNTHETIC RUBBERLIKE MATERIALS

## II. COMPOUNDED RUBBERS

C. M. BLOW, W. P. FLETCHER, AND J. R. SCHOFIELD

EVINGTON VALLEY MILLS, LEICESTER, ENGLAND

### INTRODUCTION

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In a recent paper<sup>1</sup>, a simple method has been described for the measurement of the dynamic compression modulus and associated resilience of gum stocks of natural rubber and a variety of synthetic rubbers in the temperature range of 5°–40° C. The results obtained were of sufficient interest to justify an extension of the work to compounded materials of greater commercial importance than the gum stocks of the earlier work. In particular, the aim of the present experiments has been to discover if the temperature characteristics of the gum stock of any given polymer are exhibited also by its commercial compounds, or alternatively whether normal compounding effects any considerable change in the temperature behavior of the polymer.

### APPARATUS AND METHOD OF TEST

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Details of the test method, apparatus and theory have been given in the previous paper<sup>1</sup>. The method used was based on the familiar resonance phenomenon<sup>2</sup>. The vibratory system consisted of a framework supported by the rubber samples under test, and resonance was obtained by varying the speed of the electric motor which was employed to excite vertical vibrations in the system. The vibration amplitude was measured by a vibration meter<sup>3</sup>, and the vibratory system was enclosed in a box capable of being maintained at any desired temperature in the range of 5°–40° C. The dynamic compression modulus and resilience are calculated from the measured quantities by the established formulas.

### RESULTS

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Measurements were made on natural rubber, on three types of Neoprene, on six types of butadiene-acrylonitrile copolymer, on GR-S and on Thiokol-RD (a mixed polymer of undisclosed composition). The compounding formulas for the basic stocks are shown in Table 1, all quantities being by weight. In the case of loaded compounds the loading is given as a percentage of the weight of polymer.

f

In all cases measurements were made on stocks compounded with various proportions and types of black, corresponding to the gum stocks whose properties were described in the previous paper. Before discussing the characteristics of the polymers, a word should be said about the effect of cure. At least one compound of each polymer was given a range of cures of 30, 45 and 60

TABLE 1  
COMPOUNDING FORMULAS

	Rubber	GR-S	GR-S(A)	Neo- prene- GN	Neo- prene- YD	Neo- prene-Z	Butadiene- acrylonitrile polymers
Polymer	100	100	100	100	100	100	100
Sulfur	3	3.75	3.75	...	1	1	1.5
Zinc oxide	4	6.25	6.25	1	10	5	5
Wood rosin	...	...	...	...	5	5	...
Calcined magnesia	...	...	...	4	10	10	...
Mercaptobenzothiazole	0.75	1	1	...	...	...	...
Santocure	...	...	...	...	...	...	0.75
Pine tar substitute	...	...	5	...	...	...	...
Tricresyl phosphate	...	...	...	5	5	5	20
Cottonseed oil	...	...	...	5	5	...	...
Stearic acid	1	...	...	...	...	...	1
Iranoline Rt. 2228	...	12.5	...	...	...	...	...
Mrx	...	12.5	...	...	...	...	...

minutes at 60 lbs. per sq. in. steam pressure (153° C). Table 2, which gives a few typical figures, shows the cure effect to be very small over this range; the variation is indeed within the limits of experimental error. The cure for each polymer studied was, in fact, fixed at a point on the flat portion of the modulus-time of cure curve, which also coincides with a flat portion of the resilience-time of cure curve. In most cases the cure was 30 minutes at 153° C; in the case of certain of the gas-black stocks it was 45 minutes at 153° C.

TABLE 2  
PERBUNAN (25/75) WITH 20% P-33 STOCK

	Cure: min. at 153° C				Cure: min. at 153° C		
	30	45	60		30	45	60
Dynamic modulus							
megadynes per sq. cm. at 10° C	48.8	48.7	49.7	Resilience, percentage at 10° C	46.5	48.7	46
megadynes per sq. cm. at 20° C	41.1	41.7	41.7	Resilience, percentage at 20° C	64.2	63.8	63.7
megadynes per sq. cm. at 40° C	36.2	35.6	36.3	Resilience, percentage at 40° C	67.5	67.5	68.0

NEOPRENE-Z WITH 20% GAS BLACK

	Cure: min. at 153° C				Cure: min. at 153° C		
	30	45	60		30	45	60
Dynamic modulus							
megadynes per sq. cm. at 15° C	151	148	154	Resilience, percentage at 15° C	39.0	38.5	37.7
megadynes per sq. cm. at 20° C	130	128	129	Resilience, percentage at 20° C	46.0	46.0	45.8
megadynes per sq. cm. at 40° C	100	98	98	Resilience, percentage at 40° C	73.7	75.2	74.6

As the main interest of the present work lay in the variation of modulus with temperature rather than in the absolute value of this property, the results are given in the form of relative modulus *vs.* temperature curves, the relative modulus at a given temperature being defined as the modulus at that temperature divided by the modulus at 20° C. Thus the slope of such a curve indicates the sensitivity of the property to temperature, irrespective of its absolute value, and enables one more clearly to compare materials of widely differing characteristics, *e.g.*, a rubber gum stock with a hard stock loaded with gas black.

## GUM STOCKS

The results for gum stocks, some of which were discussed in the earlier paper, are summarized by Figures 1 to 4. All the materials show a decreasing

modulus with increasing temperature, and natural rubber is prominent by virtue of its relative insensitivity to temperature. The resilience curves shown in Figure 2, take the form of two approximately linear portions of different

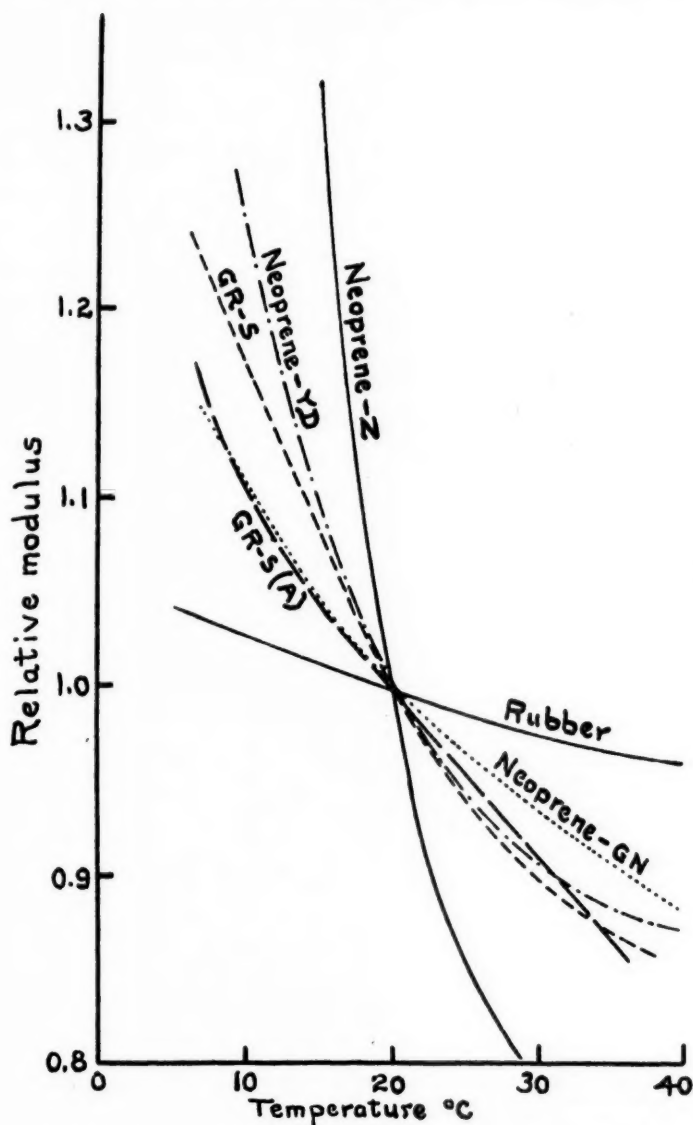


FIG. 1.—Curves of relative modulus vs. temperature for gum stocks of rubber, GR-S and Neoprenes.

slope; a similar effect has been found by Stambaugh<sup>4</sup>, working with natural rubber on an electrically excited vibrator, and by Dillon, Prettyman and Hall<sup>5</sup>, working with natural rubber and butadiene-styrene polymers.

Figure 3 shows resilience plotted against temperature for a number of butadiene-acrylonitrile copolymers (the polymer constitution being indicated in each case, the first figure indicating acrylonitrile), with the addition of

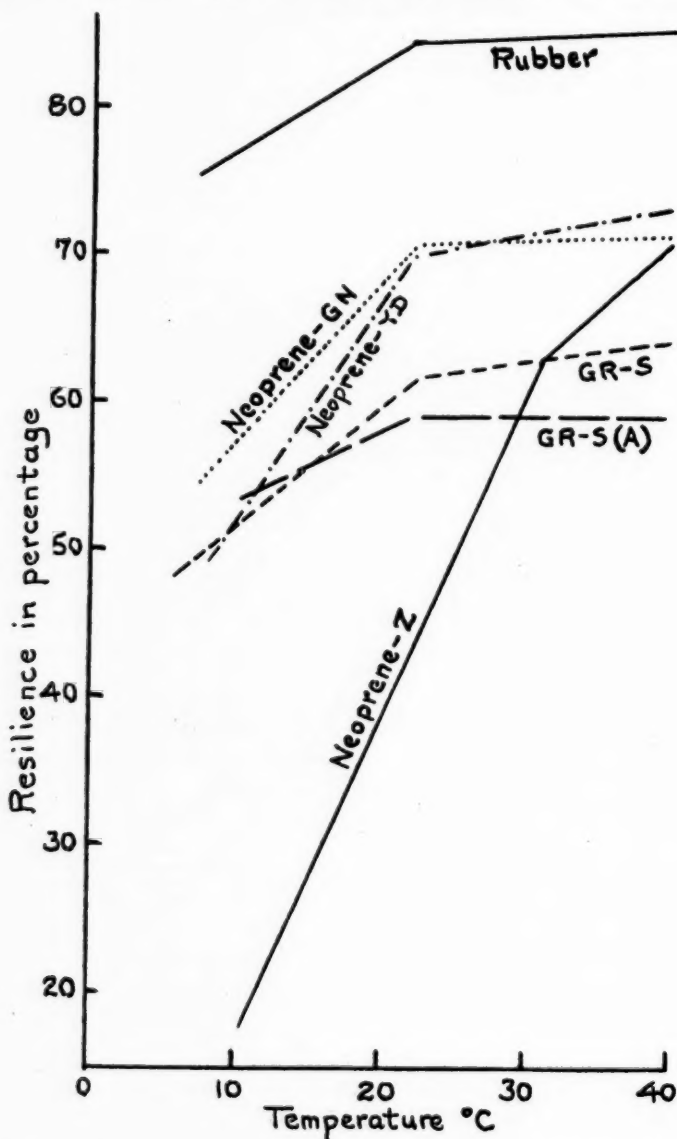


Fig. 2.—Curves of resilience vs. temperature for gum stocks of rubber, GR-S and the Neoprenes.

Thiokol-RD. Not all the curves have a sharp transition but, in general, with the exception of Thiokol-RD, they consist of two approximately linear portions of different slopes. The absence of sharp transitions may be due to inhomoge-

neity; however, it is possible by interpolation to estimate the approximate transition points. Remembering that rubber, GR-S, Neoprene-GN and -YD give transitions at 22° C (Figure 2), we now find the transition temperature

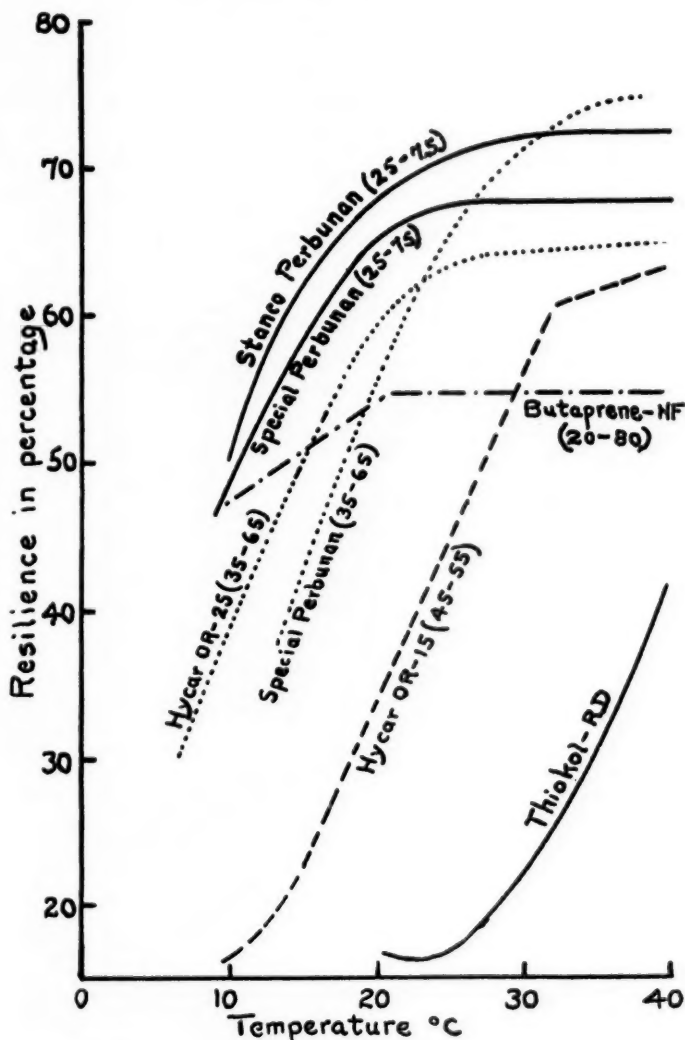


FIG. 3.—Curves of resilience vs. temperature for gum stocks of butadiene-acrylonitrile copolymers and Thiokol-RD.

shown in Table 4. Differences are observed in the curves for materials of the same stated composition, both at low and high temperatures.

The curve for Thiokol-RD shows a distinct minimum at 23–25° C; it seems that at some slightly lower temperature this polymer freezes to give modulus and resilience values commonly associated with rigid crystalline materials.

A suggestion of a similar effect is shown by the Hycar OR-15 curves; a similar result for this synthetic was found by Jones and Snyder<sup>6</sup> who used a pendulum rebound method for measuring resilience. Using a Shore scleroscope, the

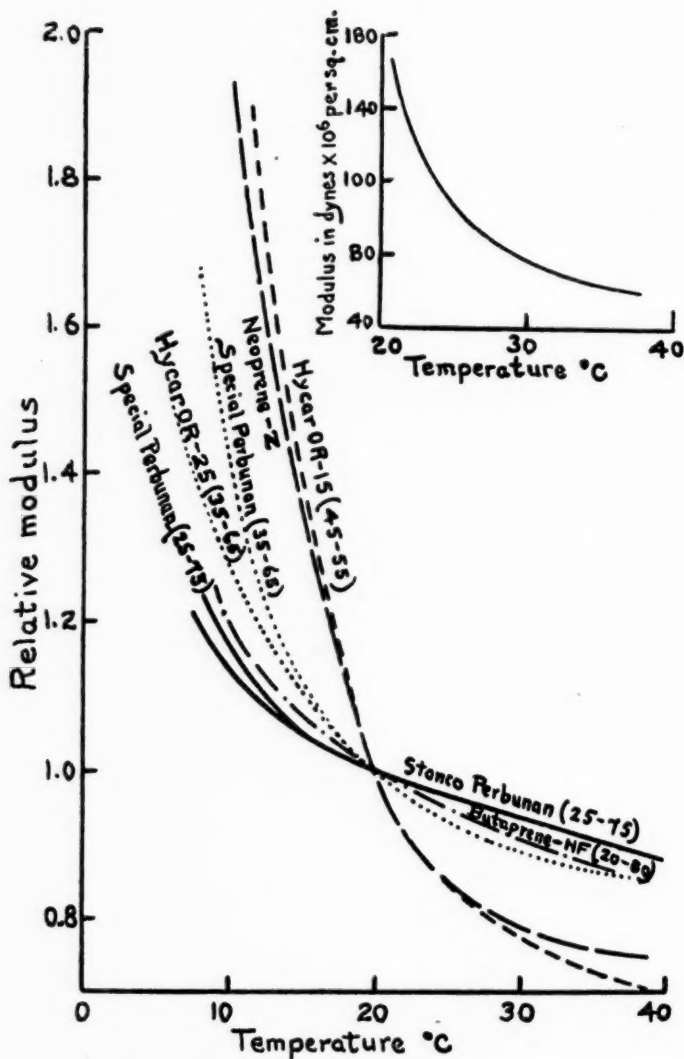


FIG. 4.—Curves of relative modulus vs. temperature for gum stocks of butadiene-acrylonitrile copolymers and Neoprene-Z. Inset modulus vs. temperature for Thiokol-RD.

Research Association of British Rubber Manufacturers' reports minima on the resilience-temperature curves of several synthetic rubbers and, on comparing these results with those at present under discussion, it seems that the temperature of the minimum point varies somewhat with the method of test, *e.g.*,

dynamic vibration test or a rebound test, a result which is not unexpected. The curve given by Jones and Snyder for Perbunan (presumably Stanco Perbunan) is very similar in shape and general level to that shown on the

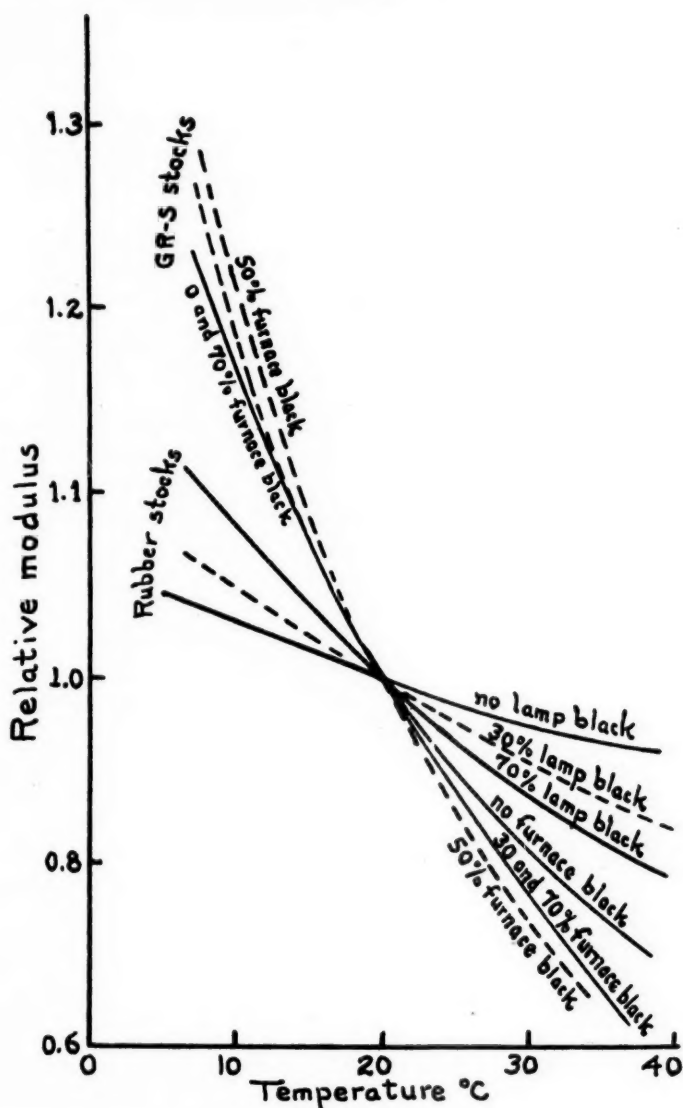


FIG. 5.—Curves of relative modulus vs. temperature for GR-S furnace-black stocks and rubber gas-black stocks, showing effects of increasing loading.

graph. It should be pointed out that results for resilience are absolute and not relative, and refer to compounds, the static and dynamic moduli of which are not coincident at any one temperature.

## STOCKS LOADED WITH CARBON BLACK

A detailed study has been made of rubber and GR-S compounds containing several types of black in various percentages. Typical curves are shown in Figures 5 to 9. For rubber, loading with lamp black gives on increasing variation in the modulus with temperature, and this is general for all natural-rubber stocks loaded with carbon black (Figure 5). The resilience value is reduced by

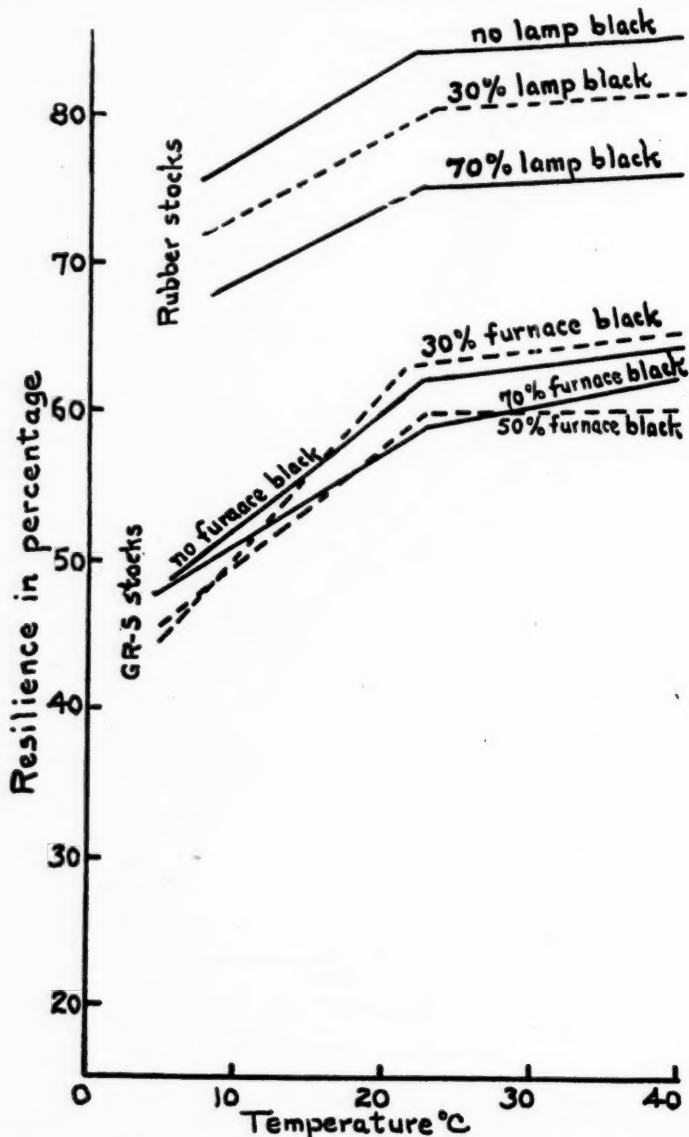


FIG. 6.—Curves of resilience vs. temperature for GR-S furnace-black stocks and rubber gas-black stocks, showing effects of increasing loading.

such loading at all temperatures, the slope and transition point of the curves appearing practically unaltered (Figure 6). Although in general loading of GR-S appears to increase its sensitivity to temperature, this is not always the

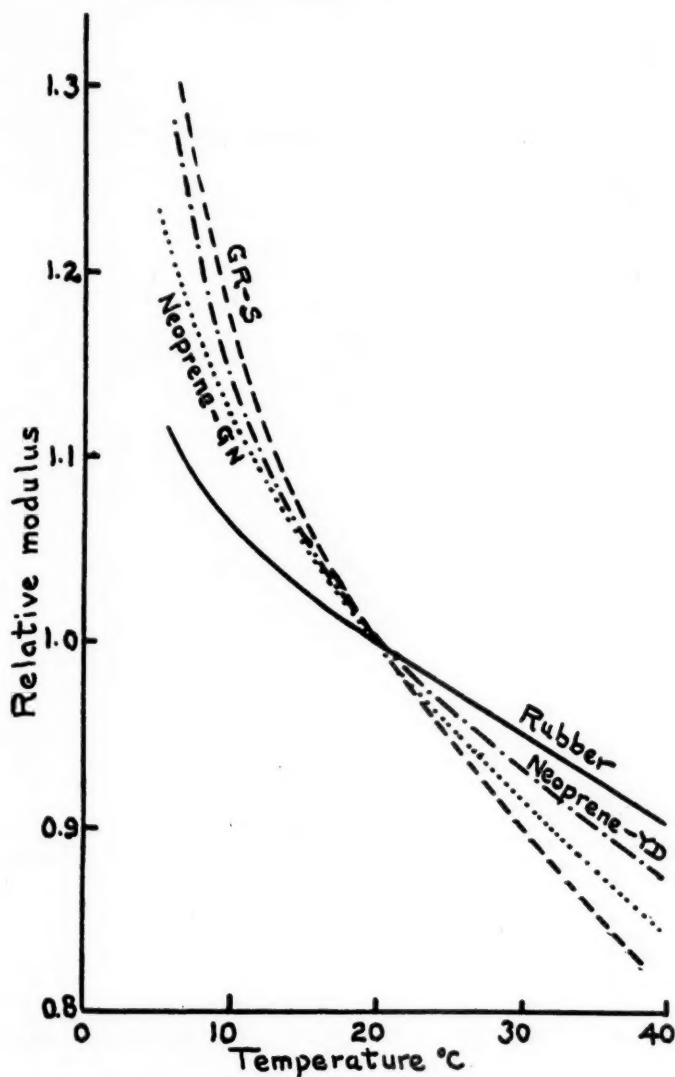


FIG. 7.—Curves of relative modulus vs. temperature for 20% gas-black stocks of rubber, GR-S and Neoprenes.

case. The results illustrated show that 50% loading of furnace black gives the highest temperature variation among the four compounds of this type. The 30 per cent stock is intermediate, while the 70 per cent stocks appear to give results coincident with the gum stock at low temperatures, but coincident with

the 30 per cent stock at higher temperature, where it is also quite close to the curve of the 50 per cent stock. A similar and somewhat random variation with loading is also exhibited in the resilience data, but the transition temperature is little if any different from that of the gum stock. In general it appears that

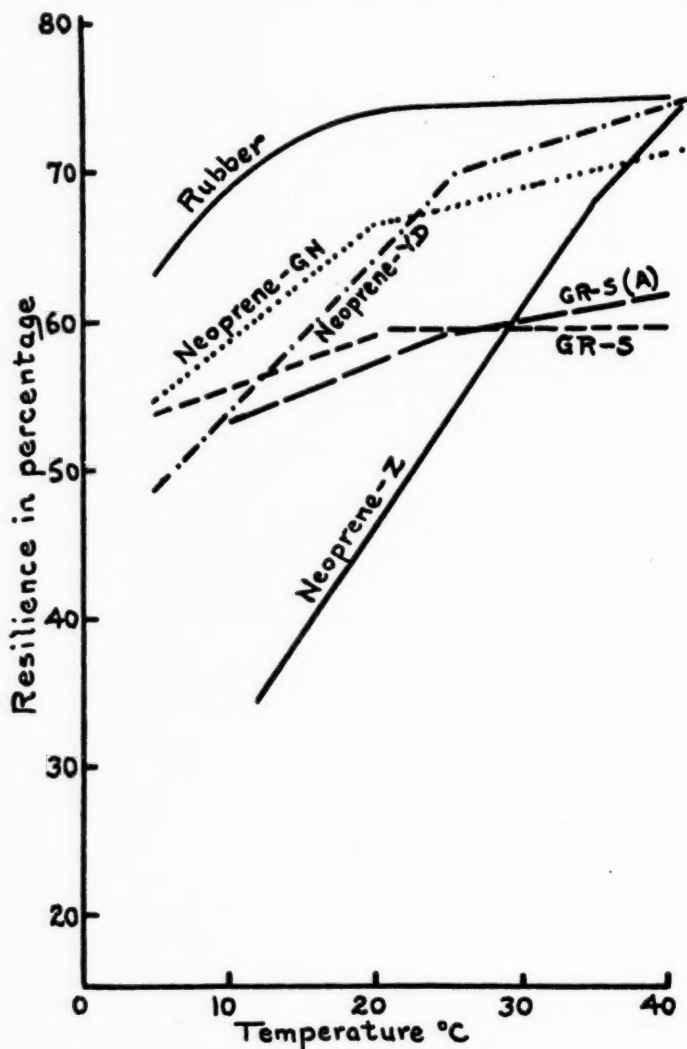


FIG. 8.—Curves of resilience vs. temperature for 20% gas-black stocks of rubber, GR-S and Neoprenes

loading of GR-S stocks causes less change, both in the relative modulus-temperature relationships and in the resilience values, than is the case with rubber. The changes seem, in fact, to be of the same order as those due to unintentional variations in the raw GR-S and its processing.

Results are next to be given for most of the polymers compounded with 20 per cent of P-33 black and 20 per cent of gas black.

The effects of 20 per cent of gas black on the modulus characteristics of rubber, GR-S, GR-S(A) and Neoprenes are seen in Figure 7; by comparison with

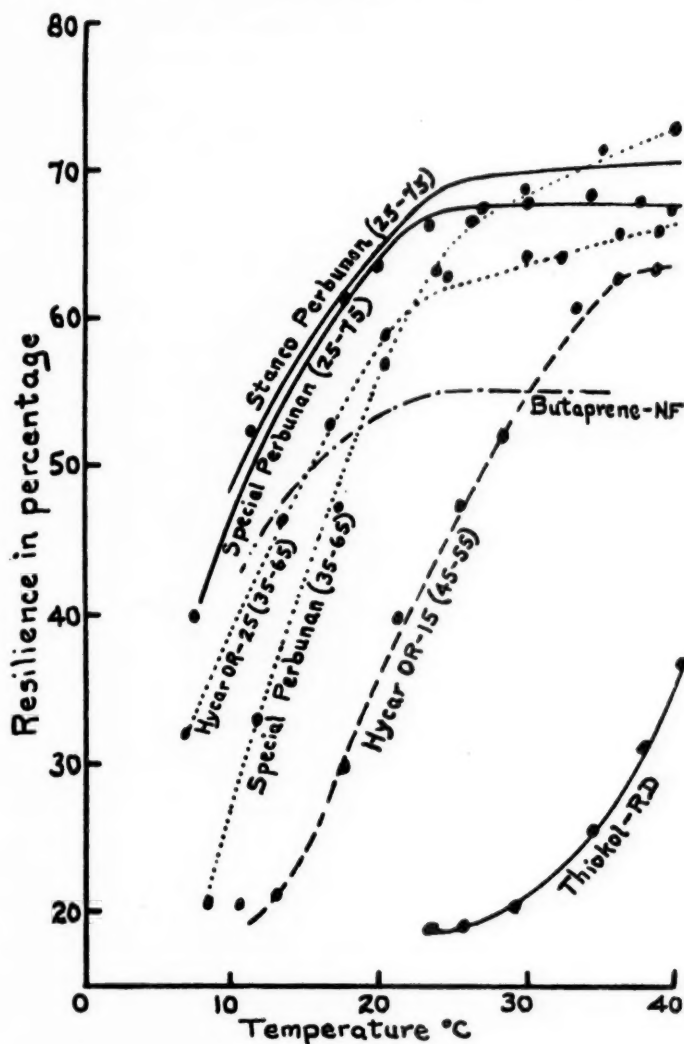


Fig. 9.—Curves of resilience vs. temperature for 20% P-33 stocks of butadiene-acrylonitrile copolymers of Thiokol-RD.

Figure 1 it is evident that the modulus temperature coefficient is almost trebled for rubber by this addition, increased by about 25 per cent for Neoprene-GN and by a similar amount for GR-S. The GR-S(A) curve for the loaded stock coincides with that for the GR-S (high extender) and thus the black loading

has masked the effect of the extender. The effect of loading Neoprene-YD is to reduce the temperature coefficient of modulus.

Table 3 gives a summary of the effects of P-33 black loading on the relative moduli of all the materials studied. In the case of 20 per cent P-33 compounds of rubber, GR-S, etc., the effect of the loading is much smaller than the effect of gas black loading. An exception is the case of rubber at the lower temperatures, where the P-33 and gas black loadings give practically identical curves. Neoprene-YD again gives an opposite loading effect from the other polymers.

The P-33 stocks of the butadiene-acrylonitrile copolymers show modulus temperature coefficients slightly greater than those of the corresponding gum stocks, the loaded stocks lying in the same order as the gum stocks. Results obtained for gas black loading of these synthetics show effects similar to the P-33 stocks.

Figure 8 shows the resilience results for the gas black compounds of rubber, GR-S, etc. The main features are that loading reduces the relative superiority

TABLE 3  
PERCENTAGE MODULUS CHANGE RELATIVE TO 20° C

	Gum stocks		20% P-33	
	10° C	30° C	10° C	30° C
Natural rubber	+ 3	- 3	+ 6	- 3
GR-S	+17	-10	+16	-11
GR-S(A)	+10	- 9		
Neoprene-GN	+11	- 7	+11	- 7
Neoprene-YD	+24	- 9	+13	- 8
Neoprene-Z	+90	-21		
Butaprene-NF	+20	- 9	+24	-14
Perbunan (Standard)	+13	- 6	+18	- 6
Perbunan (25/75)	+17	- 6	+20	- 6
Hycar OR-25	+27	-11	+30	- 8
Perbunan (35/65)	+40	-11	+49	-11
Hycar OR-15	> +100	-16	> +100	-26

of rubber, reduces the difference between extended and normal GR-S compounds, but leaves the order of the materials unchanged. The transition points between the two parts of each curve are less marked than with gum stocks, and since the transition temperatures are less easily estimated, they appear to differ slightly in some cases from those of the gum stocks. The resilience curves for P-33 stocks show similar but smaller effects of loading than the gas black loading. Figure 9 shows the effect of P-33 loading on the resilience temperature relationships in the case of the remaining polymers. There is no very marked effect; for most materials a fairly sharp transition point still exists; a series of compounds with gas black loading showed similar effects. In one case experimental points are plotted to give a fair idea of the scattering of the results throughout the experiments.

Table 4 summarizes the transition temperatures taken from the curves for all the polymers, gum stocks, 20 per cent P-33 and 20 per cent gas black loading. Gas black loading of natural rubber produces a very curved resilience temperature characteristic, and the figure of 15° C for the transition is not considered to be very reliable. The main point about these figures is that the transition temperature appears to be characteristic of the polymer, and is not greatly affected by loading. Neoprene-YD gives somewhat puzzling results, the transition temperature being reduced by P-33 loading and increased by gas black

TABLE 4  
TRANSITION TEMPERATURE °C ON RESILIENCE-TEMPERATURE CURVES

Polymer	Gum stocks	20% P-33	20% Gas black
Natural rubber	22	23	15?
GR-S	22	22	21
GR-S(A)	22	21.5	24
Neoprene-GN	22	20	20
Neoprene-YD	22	18.5	25.5
Neoprene-Z	31	..	35
Butaprene-NF	20.5	20	22
Perbunan (Stanco)	20	21.5	21
Perbunan (Special)	20	20.5	21
Hycar OR-25	21.5	21	..
Perbunan (Special)	27	24	24
Hycar OR-15	32	34	..

loading. The butadiene-acrylonitrile polymers show the effect of the composition of the polymer on the transition point. The value of 27° C for the transition point of the gum stock of Special Perbunan containing 35 per cent acrylonitrile seems anomalous.

The above curves and comments on them are typical of the results obtained in this investigation, which covered a wide range of loadings of the various blacks in the various polymers. Certain anomalous behavior has been observed which requires further investigation; in particular, the resilience temperature relation of gas black-loaded natural rubber and GR-S, which showed a reverse slope above the transition point, and also the whole of the results for Neoprene-E, as mentioned in the previous paper. Table 5 gives the 20° C

TABLE 5  
MODULUS IN DYNES  $\times 10^6$  PER SQ. CM. AT 20° C

	Base mix	20% P-33	20% Gas black
Natural rubber	20.6	27.95	38.52
GR-S	31.13	51.1	78.9
GR-S (low softener)	29.9	43.35	53.2
Neoprene-GN	28.1	41.6	55.5
Neoprene-YD	34.6	57.8	80.7
Neoprene-Z	51.3	..	129.8
Butaprene-NF	30.4	34.7	36.1
Perbunan (Standard)	32.9	41.6	51.2
Perbunan (75/25)	32.0	41.7	58.0
Perbunan (65/35)	36.6	46.7	57.3
Hycar OR-15	46.6	64.5	..
Hycar OR-25	33.7	42.8	..

Percentage of black	Natural rubber lamp black	GR-S Furnace black
0	20.6	31.1
30	51.0	64.5
50	..	110.0
70	71.3	143.5

modulus figures for those compounds whose behavior is illustrated by the graphs.

It is felt that, in passing, reference should be made to a paper recently published by Morron, Knap, Linhorst and Viohl<sup>7</sup>, entitled "The effect of temperature on the vibration characteristics of natural and synthetic rubbers". Part of this paper describes experiments in which a load is suspended from a

vibrating base by means of a shear type mounting made in one of a number of polymers. The authors measure the amplitude of vibration excited in the supported load, and, by taking the ratio of amplitude of supported body to amplitude of support, get a value for the percentage transmission of the mounting. This experimental method is simple and quite justified. However, tests are made on a series of mountings made from so-called 40 and 60 durometer commercial stocks of a number of polymers, *viz.*, rubber, GR-S, GR-M, GR-I and Perbunan, over a temperature range from 100° F down to the minimum possible temperature for each material. Curves of percentage transmission *vs.* temperature are constructed for the 40 and 60 hardness compounds, and, from the shapes and positions of the curves in each set, the authors deduce the value of the various polymers as vibration insulators. The basis of comparison is considered to be quite unjustifiable. In a given application and using a mounting of definite shape and size, the value of vibration transmission is almost entirely determined by the dynamic modulus of the rubber of synthetic used. Hence the only fair method of comparison of the temperature behavior of rubbers from this point of view is to take a series of compounds of the various materials, all having the same dynamic modulus at some standard temperature, *e.g.*, 20° C., and therefore giving the same percentage transmission at that standard temperature, and then trace the variation of the transmission as the temperature is altered.

In the paper under discussion compounds were taken, *e.g.*, for GR-I, GR-S and Perbunan, which were not suitable for the application, even at normal temperatures. The major point is that the classification of rubbers for the purpose of vibration insulation must be on a basis of dynamic modulus and not Shore hardness. The development of dynamic testing methods for rubber which took place in the 1930's was, in fact, due to the realization of this.

### CONCLUSIONS

The whole of the dynamic modulus results may be summarized as follows.

(1) A general sensitivity to temperature over the range studied is shown by all rubbers, natural and synthetic.

(2) Natural rubber is least sensitive, followed by Neoprene-GN and GR-S. Next in order come Neoprene-YD and butadiene-acrylonitrile copolymers with low acrylonitrile contents. In general, the higher the acrylonitrile content, the more sensitive to temperature is the polymer. Neoprene-Z is only slightly less sensitive than Hycar OR-15 (45-55).

(3) Broadly speaking, the effect of compounding with P-33 black and gas black is to increase the sensitivity to temperature. Notable exceptions are Neoprene-GN and GR-S containing extender, which appear almost unchanged, and Neoprene-YD, which shows a decreased sensitivity with loading.

(4) It is evident from the results that any specification for dynamic modulus should be accompanied by a specified temperature of test; in design, account must be taken of the variations which it has been shown can be quite considerable for synthetic rubbers now coming into commercial use, even under normal seasonal variation of temperature.

(5) Static methods of determining freeze points, *e.g.*, torsion and bending tests, in general place materials in a similar order with respect to their low-temperature behavior as the present dynamic experiments, although no appreciable temperature effects are noted in the temperature range of the experiments discussed here.

The results of resilience measurement are not easy to summarize. Suffice it to say that, over the limited range of temperatures investigated, very great differences in resilience are observed between different polymers. The superiority of natural rubber is again evident, although it is somewhat less marked in loaded stocks. In the case of Thiokol-RD and Hycar OR-15, minima in the resilience curves are indicated at 23° C and about 10° C, respectively. This has been reported by previous workers. In all polymers the resilience-temperature curve is in two parts, with a more or less sharply defined transition point, the temperature of which seems to depend largely on the chemical structure of the polymer. Again this is confirmed to some extent by reference to the literature.

#### ACKNOWLEDGMENTS

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# TEAR RESISTANCE

## I. MECHANISMS OF TEARING OF NATURAL AND SYNTHETIC RUBBERS \*

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### INTRODUCTION

Although natural rubber has relatively good tear resistance when reinforced with carbon black, thin rubber articles tend to tear easily, and some fillers which produce a marked grain effect in the rubber reduce the tear resistance to a low value. Tear resistance is of practical importance in such applications as tire components, inner tubes, hose and tubing, hot water bottles, and gloves. With the increased use of synthetic rubbers, which have lower tear resistance than natural rubber, this problem has become much more acute. Under certain conditions some synthetic rubbers have such low resistance to tearing as to restrict severely their use in applications where stringent service conditions are met, as, for instance, in certain classes of tires and other complicated mouldings.

As the importance of resistance to tearing in service life has been realized, so this property of vulcanized rubber has received ever-increasing attention. Crude hand-tests applied to inner tubes were the first methods of estimating tear resistance. The tubes were stretched and cut with scissors, and if the tear did not travel, the tube was considered to be satisfactory. Many quantitative methods are now in use in the rubber industry, and a résumé of these tests is given. As the experimental work in this paper raises some controversial issues, it is important that the full story of the development of tear-testing be told.

Zimmerman<sup>1</sup> was the first to publish quantitative test data on tear resistance. He measured the total work done in tearing a longitudinal slit in the center of a test slab by pulling at right angles to the slit. This author used the formula:

$$W = \frac{Ka - \frac{Fl}{2}}{Lt},$$

where  $W$  = work in inch-pounds to tear a slit 1 inch long in a slab 1 inch thick;  $a$  = area in square inches under the stress curve;  $L$  = length of torn slit in inches;  $t$  = thickness of slab in inches;  $F$  = final force in lbs., where tearing is complete;  $l$  = elongation in inches; and  $K$  = constant depending on the testing machine.

Tuttle<sup>2</sup> tested, in a tensile tester, straight test-pieces with several transverse

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cuts on one edge, and measured the elongation at the moment of break, expressing the resistance to tear in terms of percentage increase in length.

The Winkelman crescent tear test, devised by D. D. Ayres in 1927, was developed from Tuttle's work, with one important change in procedure. Although Tuttle had recognized that elongation was an important factor in tear resistance it is, as Busse<sup>3</sup>, suggested, the elongation in the region of the tear which is the important factor. With the testing methods available up to the end of 1944 this property could not be measured accurately. It may be that this was realized in 1927, for when the Winkelman tear test was introduced the force which ruptured the test-specimen was taken as the measure of tear resistance.

Wright<sup>4</sup> introduced his tongue-shear tear test but, whereas this test-piece may approximate tearing conditions more exactly, the complicated form of the test-piece does not lend itself to analysis, and the crescent-shaped test-piece gives more reproducible results.

Carpenter and Sargisson<sup>5</sup>, who were the first to describe the crescent tear test, found that the tear resistance of a given compound was a function of the state of cure, and was related to the tensile strength, the modulus, and the resistance to abrasion of the compound. In their experiments these authors used the test-piece shown first in Figure 1. The inner curve edge was nicked with five equally spaced nicks 0.1 inch apart and 0.02 inch deep.

More recently, work by Poules<sup>6</sup> has shown that the tear might start from any of the five nicks, and more reproducible results were obtained when one nick 0.02 inch deep in the center of the crescent was used.

The method of the American Society for Testing Materials<sup>7</sup> was adopted, with the single nick which permits the use of either test pieces shown in Figure 1.

Besides the crescent method there are numerous other methods for testing tear resistance, and there have been several notable papers which focus attention on the various factors affecting tear resistance. One of the most comprehensive papers discussing the mechanism of tearing is that of Busse<sup>3</sup>, who assumes rubber to be "an ideal, highly elastic medium which remains isotropic when stretched". In this case rubber has the following properties: (1) it is substantially homogeneous and isotropic even when stretched; (2) the stress-strain properties are independent of the rate of stretching; and (3) the stresses in two dimensions are not influenced by the size of the sample in the third dimension. The third condition implies that, other factors being constant, the tearing force is proportional to the sample thickness.

Experimental results given in this paper show that the third condition is not fulfilled in practice, and it is not sufficiently appreciated that the width of the sample also is a governing factor. This important point is referred to in detail in the discussion.

Busse calculates tearing to be equivalent to a very high rate of elongation (60,000 per cent per second), and his work suggests that two tests are required if tear resistance is to be evaluated adequately. First, a test is required which does not involve the cutting of the sample to begin with, as it is desirable that some measure of the force required to start the tear should be obtained. The author has found only one method<sup>8</sup> for carrying out this test. It is difficult to see how existing methods for measuring tensile strength could be modified suitably so that the stress to start a fracture could be measured. Tensile tests at either slower speeds or higher temperatures might give an indication. Secondly, a test is required which involves cutting the sample, and thus meas-

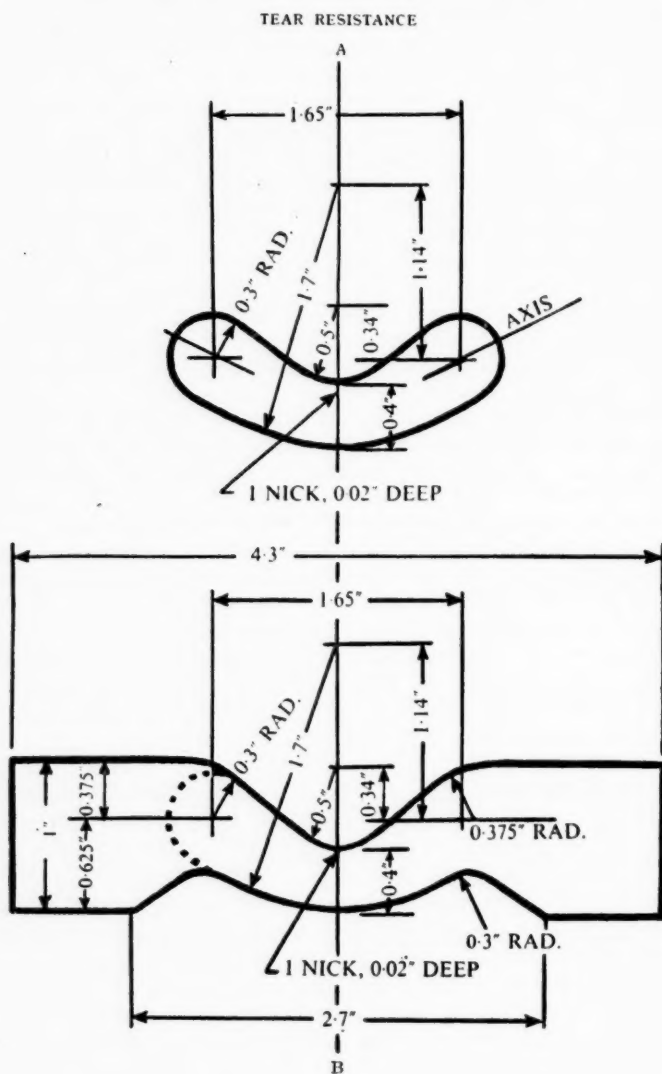


FIG. 1

ures the stress required to tear after a cut has been formed. This is the conventional tear test.

It has been pointed out<sup>3</sup> that, although it takes a considerable stress to start a tear, the stress required to make it continue is surprisingly small, due to the fact that only a very small area of rubber is being stretched. It must be emphasized that the stress referred to is the average stress over the uncut portion and not the total stress applied to the sample. The strain over the uncut portion is at a maximum when the tear starts, and decreases immediately the tear starts. Similarly the stress at the edge of the tear falls.

Clarke<sup>8</sup> describes a tear test in which, using special equipment, the tear resistance of an unnicked sample can be tested. This author describes a tear as a "type of tensile separation with the forces acting on a line, instead of over an area, as in the usual tensile break". This hypothesis may be misleading. If the classification of tear tests into the following main groups is accepted: (1) direct tearing, and (2) tearing perpendicular to the direction of stretching, the above description of a tear can apply only to the first group, where tear-testing is analogous to ply separation.

The stress-strain relationship shown in Figure 2(a) is obtained in the normal ply-separation test<sup>9</sup>, and Figure 2(b) shows a typical stress-strain relationship obtained in accordance with the Report of the American Society for Testing Materials already mentioned<sup>7</sup>. In the ply-separation test (Figure 2(a)) the stresses are acting in a line and, after the stress has reached its maximum, the time of test is the factor which governs the length of strip separated. In Figure 2(b) the stress is increasing throughout the whole of the test. The author puts forward an alternative hypothesis on the basis of this stress-strain curve.

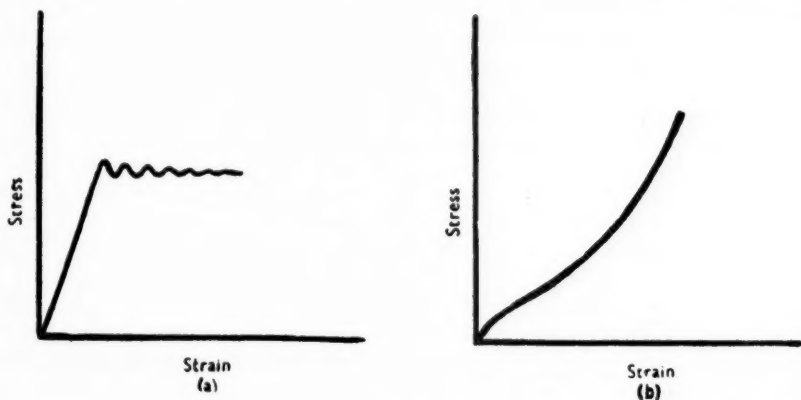


FIG. 2

Considering the crescent tear test as analogous to tensile testing, the forces act over an area. From Figure 2(b) it is seen that the stress increases progressively. As the tear proceeds, the area of the sample under stress is reduced proportionately. This means that the effective stress per unit area under tear is rapidly increased. It is suggested that the tear proceeds at an ever increasing rate due to the diminishing area producing an increased rate of loading. Under this increased rate of loading the rubber tears at a lower elongation. The results of Patrikeev and Melnikov<sup>10</sup>, when extrapolated, provide independent evidence to support this view. This hypothesis, whereby the effect of rate of loading is taken into account, not only agrees with, but explains, the fact that the overall elongation required to continue a tear is smaller than that required to initiate the tear.

It has been shown<sup>3</sup> that when a sample is nicked and a force applied there are high concentrations of stress around the weakened point. Once the tear proceeds, the average stress is reduced, and hence the average strain in the rubber is reduced. However, because of the diminishing area of the sample at the region of tearing, the rate of applying the stress increases so

rapidly that the rubber tears at a lower elongation and the rate of tearing actually increases. In some cases this can be seen visually. Butyl tread stocks provide good examples, as they have to be stretched to a high elongation to initiate the tear. Once started the tear proceeds at an ever increasing rate, and it can be seen that the rubber immediately preceding the tear is not under so high a degree of stretch. An examination of the ruptured samples also illustrates this point.

Apart from the work of Patrikeev and Melnikov<sup>10</sup> and Kusov<sup>11</sup>, there is no systematic work on the tear resistance of synthetic rubbers reported in the literature. These authors, unfortunately, have studied only one type of synthetic rubber and, therefore, for all practical purposes, comparative tear resistance data over the present range of synthetic rubbers are not available.

Several factors, such as thickness of sample, depth of nick and the number of nicks, affect the tear resistance of the rubber. The effect of these factors on tear resistance (measured by the American Society for Testing Materials method<sup>7</sup>), has been determined with natural rubber, but there are little published data to show how these factors affect the tear resistance of synthetic rubbers. Although it was accepted that the method above could be used to give comparative data it was considered that the permissible range of 20 per cent for individual tests was too large for a standard routine test.

The aims of this work were, therefore, three-fold: (1) to devise more accurate methods of carrying out tests than the method of the American Society for Testing Materials<sup>7</sup>; (2) to provide comparative and systematic data on natural rubber and a range of synthetic rubbers; and (3) to investigate the effect of several variables on the tear resistance of natural and synthetic rubbers, including an investigation of the effect of temperature of test.

*Effect of width of sample.*—This factor has not received adequate attention in the literature, and it is not generally appreciated that tear resistance increases with the width of the test-piece in group 2 tests. This is important when data obtained on different shaped test-pieces are being compared and also when a study of the effect of depth of nick is being made. The previous discussion has shown that tear tests are analogous to tensile tests, and it is now suggested that results should be expressed in similar units. The American Society for Testing Materials<sup>7</sup> specifies that results should be expressed as load per unit of thickness. Experimental results in this report show that it is more accurate to express results as load per unit of thickness  $\times$  width. In the discussion, it is shown that a few anomalous results suggest that a still more accurate basis would be one where results are expressed as follows:  $T = \frac{L}{t \times D}$ ,

where  $T$  = tear resistance in Kg. per sq. cm.;  $L$  = applied load in kg.;  $t$  = thickness in cm.; and  $D$  = distance tear travels in cm.

In this way some of the cases where "knotty" tears have been found can be accounted for more accurately, but sufficient results are available to show that anomalous values would still be obtained in certain cases. In most cases where exceptionally long paths have been followed, this method of calculating the results give results below the average. This is not surprising when it is considered that the development of knotty tears in crescent test-pieces gives rise to peculiar and complicated stress and strain distributions. Further progress in the explanations of knotty tears will be difficult until a full physical and mathematical analysis of the stress and strain distributions of the rubber under test conditions is made. The experimental results given in this paper place on

record some types of rupture which should be useful in elucidating and formulating the problem.

## EXPERIMENTAL

Throughout this work the following range of rubbers was studied in both gum and tread stocks, natural rubber, Neoprene-GN, GR-S, Butyl, Novoplas-A and Vulcaprene-A.

The following mixes were used:

	J. 6790	6791	6792	6793	6794	6795	6796	6797	6798	6799	6800	6801
Smoked sheet rubber	100	100	—	—	—	—	—	—	—	—	—	—
Neoprene-GN	—	—	100	100	—	—	—	—	—	—	—	—
GR-S	—	—	—	—	100	100	—	—	—	—	—	—
Butyl	—	—	—	—	—	—	106.5	106.5	—	—	—	—
Novoplas-A	—	—	—	—	—	—	—	—	100	100	—	—
Vulcaprene-A	—	—	—	—	—	—	—	—	—	—	100	100
C-35978	—	—	—	—	—	—	—	—	—	—	—	—
Zinc oxide	5	5	1	1	5	5	—	—	10	10	—	—
Stearic acid	3	3	2.5	2.5	2	2	3	3	1	1	0.5	0.5
Tricresyl phosphate	—	—	4	4	—	—	—	—	—	—	—	—
Magnesium oxide	—	—	4	4	—	—	—	—	—	—	—	—
Pine tar	—	—	—	—	3	3	—	—	—	—	—	—
Kosmos-T	—	47.5	—	36	—	50	—	70	—	—	—	—
Kosmos-20	—	—	—	—	—	—	—	—	—	25	—	—
P-33	—	—	—	—	—	—	—	—	—	—	—	60
Sulfur	3	3	—	—	2	2	0.5	0.5	—	—	—	—
Mercaptobenzo-thiazole	0.85	0.85	—	—	—	—	0.5	0.5	—	—	—	—
Nonox-S	—	—	2	2	—	—	—	—	—	0.5	—	—
Vulcafor-F	—	—	—	—	1.5	1.5	—	—	—	—	—	—
Tetramethylthiuram disulfide	—	—	—	—	—	—	1	1	—	—	—	—
J-550	—	—	—	—	—	—	—	—	—	—	5.5	5.5
C-22105	—	—	—	—	—	—	—	—	—	—	1.5	1.5

Twenty-four 2-mm. sheets of each mix were cured. This enabled six repeat tests to be done, which was considered sufficient to assess accurately the effect of each variable.

*Test Procedure.*—Using the standard (American Society for Testing Materials) die, as in Figure 1b, six test-pieces were cut from each sheet. The six test pieces were prepared as follows:

Depth of Nick: 0.1, 0.02, 0.05, 0.07, 0.10, 0.20 inch  
Sample No: 1 2 3 4 5 6

The 24 sheets were marked with the letters A to X.

Samples marked A to F were tested at room temperature; G to L at 50° C; M to R at 70° C; and S to X at 100° C.

*Testing at elevated temperatures.*—Tests were carried out on a Goodbrand tensile tester. Since a temperature jacket fitting that machine was not available when this work was done, it was only possible to use cruder methods of temperature control. The samples were wrapped in cotton wool and heated for one hour in an oven at the appropriate temperature; the removal from the oven, transfer to the Goodbrand, and the actual testing were carried out as quickly as possible.

*Method of nicking the sample.*—The American Society for Testing Materials does not give details of the method for nicking the samples, and there are no

limits of accuracy given for the depth of nick. The latter point is a definite gap in the specification.

A holder and cutter was designed for nicking the rubber samples and is shown in Figure 3. The sample is held firmly in position by means of the strong

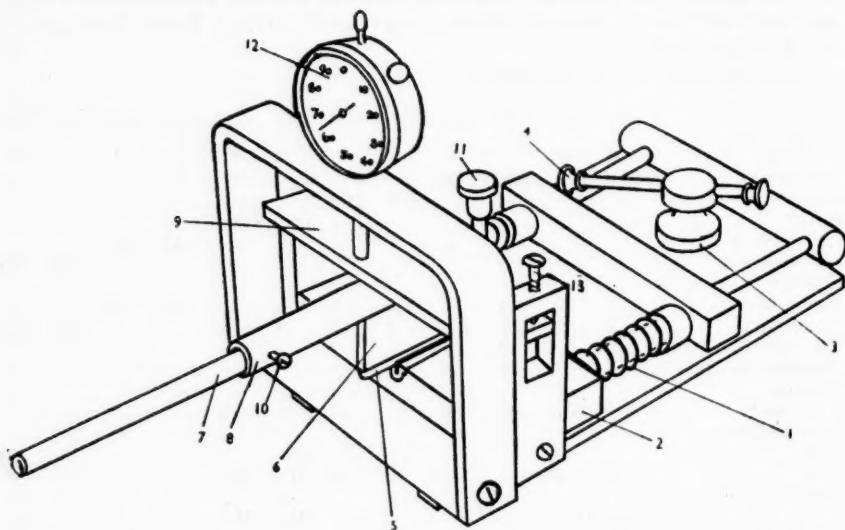


FIG. 3

springs (1). The rear portion of the holder (2) is movable and is drawn back against the springs (1) by turning the eccentric wheel (3) by the rod (4). The razor blade (5) is clamped in the holder (6) attached to rod (7), which slides along tube (8) attached rigidly to the platform (9). The rod (7) is grooved so that it can move over the projection of set-screw (10) inside the tube (8). This prevents the razor blade holder being moved in a horizontal plane. The height of the razor blade holder is altered by raising or lowering platform (9) by means of the thumb screws (11). The height of the platform

TABLE 1  
EFFECT OF DEPTH OF NICK (IN.) ON TEAR RESISTANCE (KG. PER CM.)  
AT ROOM TEMPERATURE

Depth of Nick	0	0.02	0.02	0.05	0.07	0.10	0.20
Natural Rubber Gum	104	51.3	54.2*	46.2	36.8	18.06	4.8
Tread	175	115.2	121.6*	96.8	87.2	54.6	20.5
Neoprene-GN Gum	105	43.6	46.1*	26.1	35.1	10.53	4.7
Tread	193	77.1	81.5*	58.2	49.5	35.0	17.7
GR-S Gum	13.1	5.2	5.48*	6.4	5.17	3.33	1.99
Tread	161.2	39.0	41.3*	30.5	33.8	23.8	35.9
Butyl Gum	61.7	21.5	22.7*	5.45	20.5	5.5	1.8
Tread	131	70.3	74.2*	70.0	68.0	53.5	33.8
Novoplas Gum	8.1	4.25	4.46*	4.7	4.11	2.28	1.09
Tread	20.6	14.13	14.9*	15.3	11.4	10.9	6.3
Vulcaprene Gum	43.0	26.5	27.9*	6.9	6.6	5.73	2.05
Tread	132.3	36.0	38.0*	31.1	31.1	19.48	8.7

\* Kg. per sq. cm.

is set by means of the dial gauge (12) which reads in 1/1000ths of an inch. After setting the platform it is clamped firmly in position by means of the screws (13).

*Experimental Results.*—Six test-pieces were tested at each condition of test. Table 1 shows the effect of depth of nick on the tear resistance of each rubber and Table 2 the effect of temperature on the tear resistance of each rubber. In Tables 1 and 2 the average values of the six results have been given.

TABLE 2  
EFFECT OF TEMPERATURE ON TEAR RESISTANCE (KG. PER CM.) WITH  
DEPTH OF NICK 0.02 IN.

Temperature °C	25	50	70	100
Natural Rubber Gum	51.3	56.5	56.0	43.0
Tread	115.2	89.7	75.8	60.5
Neoprene-GN Gum	43.6	18.1	8.03	4.0
Tread	77.1	74.7	47.7	30.3
GR-S Gum	5.2	6.3	5.02	3.7
Tread	39.0	42.8	47.1	26.8
Butyl Gum	21.5	4.2	4.3	2.08
Tread	70.3	66.6	67.0	58.7
Novoplas Gum	4.25	3.07	2.65	1.66
Tread	14.13	4.97	6.68	4.71
Vulcaprene Gum	26.5	15.7	9.9	11.8
Tread	36.0	27.5	17.5	15.15

Figures 4, 5, 6, 7, and 8 show the effect of depth of nick at each temperature for tread stocks of natural rubber, Neoprene-GN, GR-S, Butyl, and Vulcaprene-A, respectively.

*Effect of depth of nick.*—With all the rubbers tested, gum and tread stocks, the largest difference in tear resistance occurred between the unnicked samples and those having a nick of 0.02 inch. The tear resistance falls progressively as the depth of nick is increased up to a depth of 0.20 inch, but the rate of all is much slower than initial rate between 0.00 inch and 0.02 inch. It, therefore, appears that the initial nick of 0.02 inch is the main contributory factor towards tear resistance, results being so much lower than the normal tensile strength results.

Table 3 illustrates that the extent of fall in strength introduced by the 0.02 inch nick depends on the material being tested.

TABLE 3

Tread stocks	Depth of Nick (inch)		
	0.00	0.02	0.20
Natural rubber	175	112	20.5
Butyl	131	73.3	33.8
Neoprene-GN	193	77	17.7
GR-S	161	39	35.9
Vulcaprene-A	132	36	8.7
Novoplas-A	20.6	14.1	6.3

The above table emphasizes that nicking the sample introduces artificial conditions, which means that the results can be used only for comparative purposes and not as accurate criteria foretelling how a particular rubber behaves in service.

Patrikeev and Melnikov<sup>10</sup> found that the tear resistance of samples of natural and synthetic rubber (sodium-butadiene polymer U.S.S.R.) depended

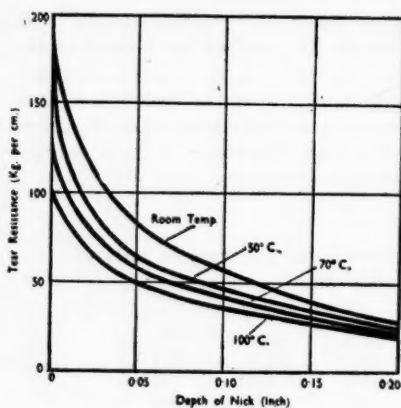


FIG. 4.—Natural rubber tread.

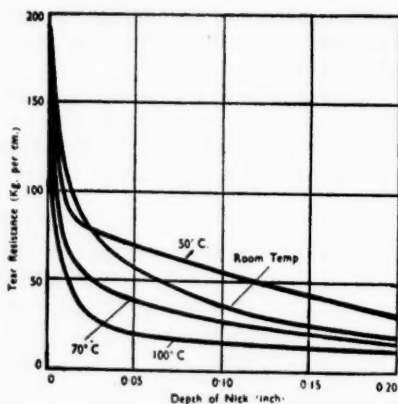


FIG. 5.—Neoprene GN.

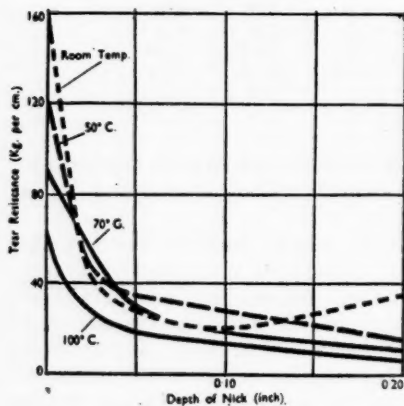


FIG. 6.—GR-S tread.

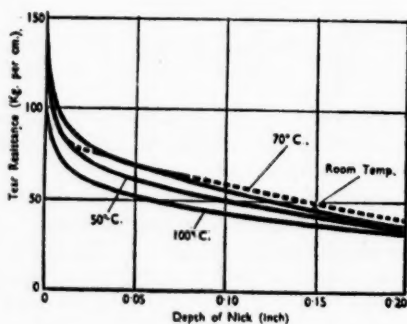


FIG. 7.—Butyl tread.

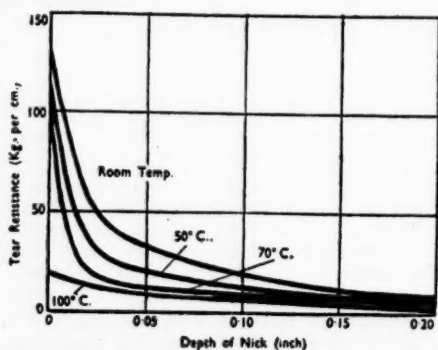


FIG. 8.—Vulcaprene tread.

on the depth of the initial cut. These authors reported that, with short cuts, natural rubber had a higher tear resistance than the synthetic rubber, but this

difference decreased as the cut was increased. The results given in Table 3 confirm these findings for all the synthetic rubbers tested in this work.

*Effect of temperature of test.*—Before discussing the effect of temperature of test on tear resistance, it is of interest to recapitulate the present theories of tear resistance.

Many authors have contributed towards our present picture of tear resistance. It is agreed that the rubber sample tears at the point where there is maximum deformation. This occurs at the base of the cut, and Busse found that the degree of maximum local deformation required to produce a tear is less than that required for a tensile break. It has been postulated that a local weakness occurs in the material at the point of tearing.

When rubber is deformed or stretched, Katz<sup>13</sup> found that an x-ray spot diagram was formed as if oriented crystals were present when the rubber is submitted to a sufficient degree of stretch, 200 per cent for vulcanized rubber.<sup>14</sup> The position of the spots, being independent of the degree of stretching, supports the view that oriented crystals are present. The intensity of the spots, however, increases with the degree of stretch. A study of the proportion of crystalline and amorphous components in stretched rubber by means of x-rays has been made by Field<sup>15</sup>, who concludes that crystallization is an important factor in maintaining the relatively high strengths of vulcanizates at high elongations. In some synthetic rubbers (GR-S) crystallization is impossible because of the random arrangement of the atoms in the molecule of the interpolymers. In this case, however, it is considered that orientation of the molecules is still possible. If Field's hypothesis is accepted it would be expected that rubbers which crystallize at high elongations would have higher tensile strengths and tear resistance than those which could only be oriented. Tests carried out at elevated temperatures support this view, and the results given in Table 4 illustrate this point.

TABLE 4  
(KG. PER CM.) WITH 0.02 INCH NICK

Tread stocks	Room Temperature	50° C	70° C	100° C
Natural Rubber	115.2	89.7	75.8	60.5
Butyl	70.3	66.6	67.0	58.7
Neoprene-GN	77.1	74.7	47.7	30.3
GR-S	39.0	42.8	47.1	26.8
Vulcaprene-A	36.0	27.5	17.5	15.15
Noyoplas-A	14.1	4.97	6.68	4.71

The first three rubbers crystallize, and have superior tear resistance at room temperature to the latter three. With slight deviations the tear resistance falls as the temperature is increased, and the extent of fall in the tear resistance of the different rubber varies with each one. Whereas natural rubber and Butyl have still relatively good tear resistance at 100° C, there has been a large decrease in the case of Neoprene-GN. Although GR-S has poor cold tear resistance, it is as good as Neoprene-GN when tested at 100° C. This important point emphasizes why it is essential that service conditions are accurately known.

Fielding<sup>16</sup> found that natural rubber and Butyl are strengthened in the direction of stretching and weakened in the other direction. He demonstrates this by stretching the rubber and tearing across and along the grain. These effects were not found with GR-S which does not crystallize.

The results quoted in Table 4 deserve close attention. Butyl rubber crystallizes and would therefore be expected to show a relatively large drop in tear resistance on raising the temperature to 100° C. However, the results show that the tear resistance of Butyl rubber is maintained at these elevated temperatures. The explanation of this phenomenon is obtained from a study of the type of tear obtained with Butyl rubber at elevated temperatures. In general, two types of tear are found; first, a straight tear where the tear proceeds in the direction of the original cut or at a slight angle to it; and secondly, a knotty tear where the sample tends to tear at right angles to the direction of the original cut. In practice a series of small tears parallel to the direction of the stretching forces appears before the tear finds the weakest path and ruptures the sample.

*Two types of tearing.*—In Figure 9 the natural rubber sample Q3 shows the straight tear which is obtained with most compounds. Sample M3, however, shows a knotty tear. It is surprising to find such a break in the case of a gum stock, for this effect has only been noted for carbon black stocks previously<sup>3</sup>. Using the Kusov type of test-piece<sup>11</sup> the phenomenon was only observed in compounds containing not less than 20 per cent of carbon black, in the presence of zinc oxide. Sample M3 was the only gum stock showing this phenomenon, but it should be recorded, for the tendency of previous authors<sup>17</sup> has been to attribute the effect to carbon black enhancing structural orientation.

Figures 10 and 11 show how, in some cases, a knotty tear develops in natural rubber after part of the sample has been torn. In Figure 11 both samples of natural rubber tread show a knotty tear with an exceptionally long path before rupture. In almost all cases (there were several exceptions) where knotty tears were found, the value of the tear resistance was higher than in the cases where a straight tear was found. When a tear changes direction at right angles the local deformation at the point of tearing is reduced considerably. This means that the deformation must be built up to the required maximum again before tearing continues; hence the higher values found with knotty tears. Under certain conditions, a force 1.5 to 2.0 times the normal force had to be applied to continue a knotty tear.

Patrikeev and Melnikov<sup>10</sup> state that knotty tearing is reduced by increasing the speed of testing, and this statement is in agreement with the present results, for increasing the speed of testing is equivalent to lowering the temperature<sup>18</sup>. It has been found in this work that knotty tearing is accentuated by raising the temperature (equivalent to decreasing the speed of testing). This is illustrated most clearly in Figures 12, 13, 14, which show the types of knotty tear obtained with Butyl tread stocks at elevated temperatures. All the samples show marked lateral tearing in the direction of the applied force. It is significant that no evidence of such tears was obtained with the samples of Butyl tread tested at room temperature.

The effect was seen when the temperature was raised to 50° C, and was more frequent at the higher temperatures. The effect appeared to be accentuated with depths of nick of 0.05 and 0.07 inch, representative samples of which are shown in the figures, but the effect was found with all depths of nick from 0.02 to 0.20 inch.

As this knotty type of tear occurred in more than 50 per cent of the samples tested, it explains how the tear resistance of Butyl rubber tread is maintained at elevated temperatures.

All the Butyl gum stocks tested showed a straight tear of the type shown in Figure 9 (sample Q3).

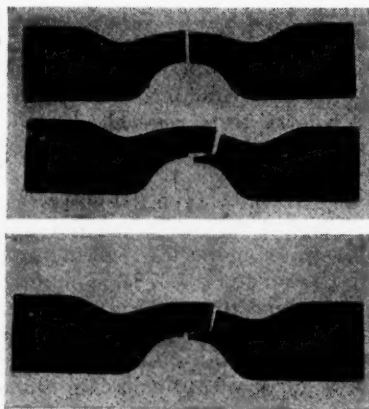


FIG. 9.—Natural rubber gum.

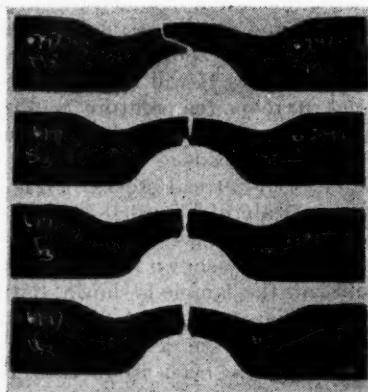


FIG. 12.—Butyl tread.

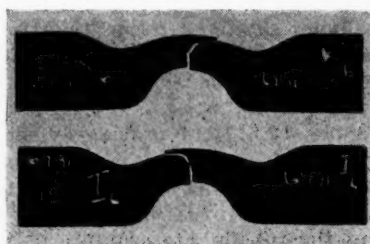


FIG. 10.—Natural rubber tread.

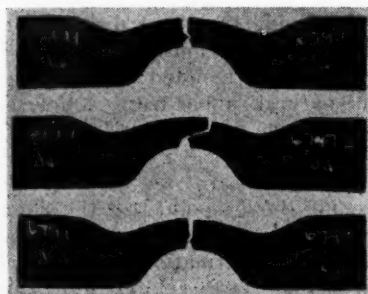


FIG. 13.—Butyl tread.

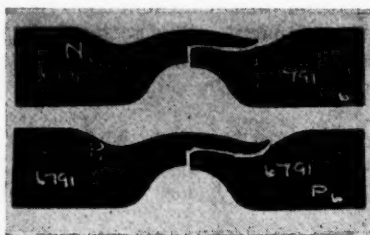


FIG. 11.—Natural rubber tread.

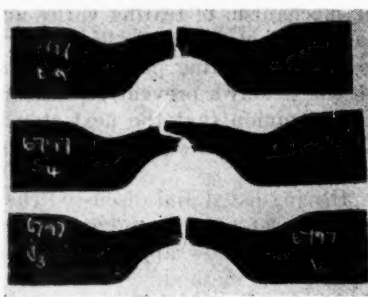


FIG. 14.—Butyl tread.

The samples shown in Figure 15 are Novoplas-A treads. A special kind of knotty tear is present in these cases. With normal knotty tears the lateral tearing proceeds from the base of the initial cut, but with Novoplas-A, at elevated temperatures, the tear tends to proceed straight and then numerous short lateral tears are formed before the straight tear continues to rupture.

These effects were noted only at temperatures of 50° C and 70° C. A temperature of 100° C is too high for this material, which tends to be thermo-

plastic, and when it is deformed at such a high temperature it has almost no strength and exhibits straight tearing in all cases.

The samples shown in Figure 16 are Neoprene-GN treads, and show typical knotty tears. It will be noted that knotty tears are obtained with this material at room temperature (sample A4). Knotty tears were also found at room temperature with natural rubber and GR-S, but not with Butyl and Novoplas-A treads.

The GR-S tread stocks in Figures 17 and 18 show typical knotty tears. A close study of Figure 18 shows the curved lateral tear which has developed in the three samples shown. This point is illustrated more clearly in Figure 19.

The sample shown in Figure 19 is a GR-S tread stock J.6795, sample D.5. Only half the sample is shown, but the curved lateral tear, typical of the samples in Figure 18, is clearly illustrated. The main interest in sample D.5 however, is in the deformation of the inner layers of the rubber. A herring bone effect has been produced. The cause is not known, but it is presumed that the stress concentrations have been greater at the inner layers than at the surface. If the stress distribution is not even throughout the thickness of the sample (as is suggested by sample D.5), the question of accurately analyzing and defining the stress distributions becomes even more vital than has been appreciated previously.

It has been noted before that some samples shattered rather than tore. The natural rubber tread sample W4 shows this type of fracture (Figure 20). This sample suggests also that the stress distribution has been greater at the inner layers.

*Elongation required to start a tear.*—Figures 12, 13, 14 provide excellent proof of Busse's point that the elongation required to start a tear is many times greater than that required to continue the tear. The rubber has been subjected to greater deformations in the region of the initial cut, as a higher degree of permanent set is exhibited by this part of the rubber after rupture of the specimen.

The preceding facts and discussion on temperature of test emphasize that the mechanism of tearing varies across a series of rubber. It is evident that many anomalous results have still to be explained satisfactorily. A study of the type of tearing produced can avoid inclusion of such anomalous results, but this is only a preventive measure and not a panacea. The author is firmly of the opinion that the next step is the mathematical and physical analysis of the stress and strain distributions encountered in the samples under test conditions.

Having listed and discussed the types of fracture prevailing when the tear resistance of natural and synthetic rubbers is measured using the A.S.T.M. method, it is now appropriate to evaluate fully and discuss the merits and value of this method.

*Discussion of A.S.T.M. method of test.*—The preceding discussion has emphasized that care must be exercised when analyzing results obtained with the A.S.T.M. method of test, as the mechanism of tearing is not the same for all the rubbers. It was presumed that the A.S.T.M. method gave the optimum testing conditions for natural rubber, and a statistical analysis of the results was carried out to verify whether the same conditions held for the other rubbers.

The individual results for each rubber were analyzed and the effects of the two main variables (temperature and depth of nick) separated. The average value and the variance<sup>19</sup> were calculated from the six repeat results at each condition of test. The standard deviation, which is the variance, was then

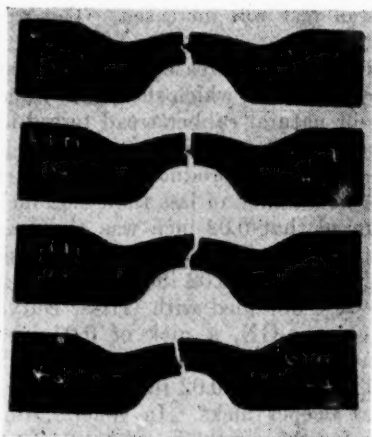


FIG. 15.—Novoplas-A tread.

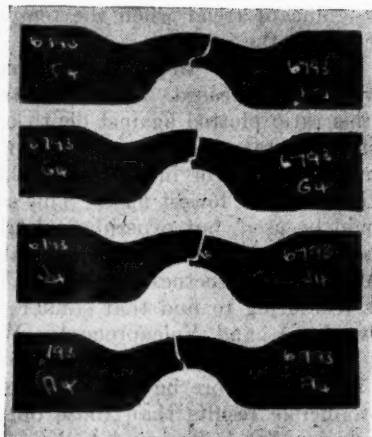


FIG. 16.—Neoprene-GN tread.

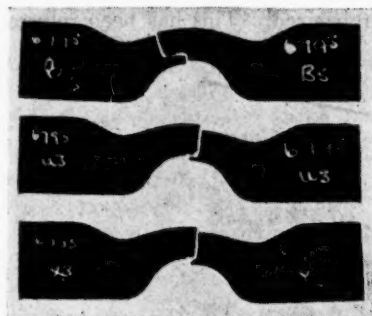


FIG. 17.—GR-S tread.

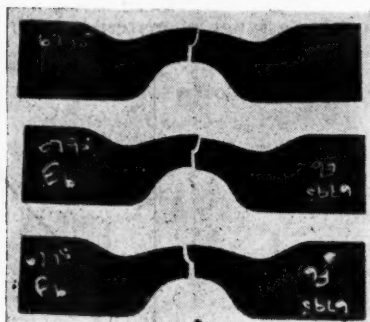


FIG. 18.—GR-S tread.

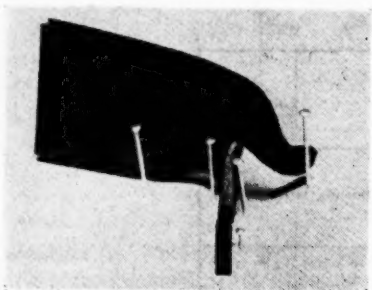


FIG. 19.—GR-S tread (J. 6795-D.5).

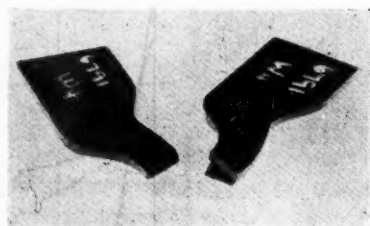


FIG. 20.—Natural rubber tread.

found and the statistical quantity, known as the coefficient of variation (standard deviation/average value) was calculated.

The value of the coefficient of variation can be taken as a measure of the repeatability of the test at each condition of test.

*Temperature of test.*—It was noted that the coefficient of variation showed

no significant trend when the temperature of test was increased. This applied to all the rubbers.

**Depth of nick.**—In general, as the depth of nick was increased the coefficient of variation increased. This is illustrated by Figure 21, which shows the value of this ratio plotted against depth of nick for natural rubber tread tested at room temperature. It is seen that the introduction of a nick into the sample introduces an error into the method, and the most reproducible results are obtained at the lowest nick. This suggests that a nick of less than 0.02 inch should be used, but experimental trials showed that 0.02 inch was about as small as could be achieved comfortably in practice. This method of analysis confirms the correctness of the A.S.T.M. choice of the 0.02 inch nick, and it was reassuring to find that similar curves were obtained with GR-S, Butyl, Novoplas-A, and Vulcaprene-A. With Neoprene-GN, a nick of 0.07 inch tended to give more reproducible results, but this may not be significant.

It can therefore be said that the A.S.T.M. nick of 0.02 inch gives more reproducible results than those obtained at deeper nicks. In general, this conclusion has been found to hold equally for the synthetic rubbers tested as for natural rubber.

The danger inherent in fixing an arbitrary depth of nick in the conditions of test for a range of materials must be emphasized. This has been referred

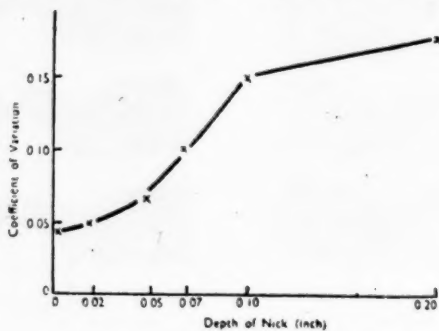


FIG. 21

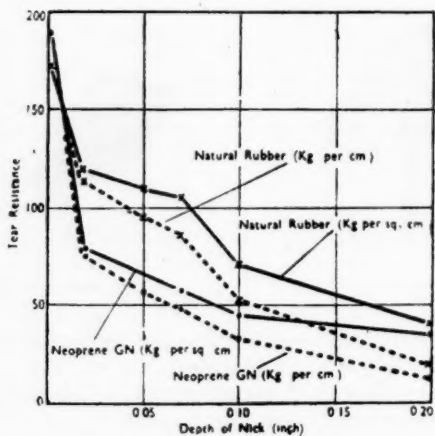


FIG. 22.—Tread stock.

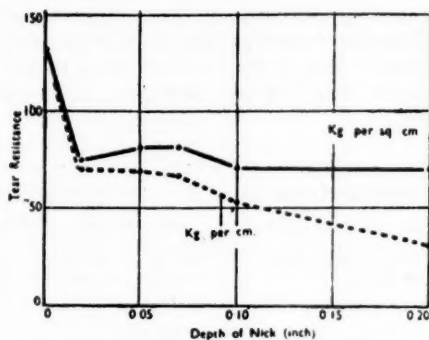


FIG. 23.—Butyl tread stock.

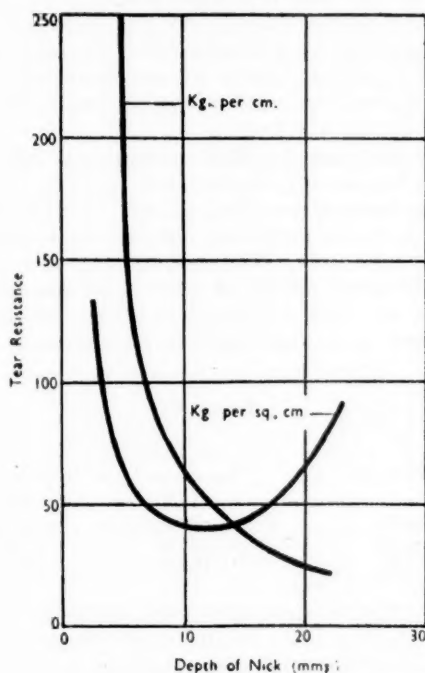


FIG. 24

to earlier in Table 3, where it was shown that the introduction of the 0.02 inch nick placed natural rubber as superior to Butyl and GR-S, whereas an increase in depth of nick to 0.20 inch made natural rubber inferior to these two synthetics.

*Error of test.*—The error of test was obtained from the coefficient of variation. The error of test obtained with natural rubber was  $\pm 12$  per cent. The position with the synthetic rubbers is not so satisfactory, however, for in each case the error of test found was  $\pm 22$  per cent.

*Effect of speed of test.*—The A.S.T.M. specification states that the rate of separation of the lower jaw should be 20 inches per minute. The experimental work in this report was carried out on a Goodbrand tensile machine, where the

highest speed is 400 mm. per minute and all the tests reported were carried out at this speed. To show the extent of the effect of speed of testing tread stocks of natural rubber, GR-S, and Butyl rubber were tested on the Goodbrand machine at three speeds, 400, 200 and 100 mm. per minute. The results are given below in Table 5

TABLE 5  
EFFECT OF SPEED OF TESTING ON TEAR RESISTANCE (KG. PER CM.)

Speed (mm. per min.)	400	200	100
Natural rubber tread	124.5	132.6	130
GR-S tread	54.6	59.8	61.4
Butyl tread	80.6	88.2	85.3

As the differences in the results are not significant, it would appear that increasing the rate of stretching from 100 mm. per minute to 400 mm. per minute has little effect on the value of the tear resistance. Other authors<sup>10</sup>, have reported that little change is observed over the range 200 to 600 mm. per minute. This means that the speed of 400 mm per minute on the Goodbrand machine can be considered approximately equivalent to the speed of 508 mm. per minute specified by the A.S.T.M.<sup>7</sup>

*Expression of results.*—The A.S.T.M. recommends that tear resistance results be expressed as kg. per cm., that is load/thickness of test-piece. It was felt that the distance the tear travelled, i.e., the width of the sample was also a governing factor, and this point was checked by testing strips of natural rubber  $\frac{1}{4}$ ,  $\frac{1}{2}$ ,  $\frac{3}{4}$ , and 1 inch wide. The samples were nicked, and the depth of nick measured accurately by means of a travelling microscope. The area of the unnicked portion was then calculated and the results expressed as kg. per sq. cm. A comparison of the two methods of expressing the results is given in Table 6.

TABLE 6

Width of sample	Tear resistance	
	Kg. per cm.	Kg. per sq. cm.
$\frac{1}{4}$ inch	45.3	71.9
$\frac{1}{2}$ inch	89.5	71.9
$\frac{3}{4}$ inch	121.0	63.9
1 inch	163.2	64.2

It is seen that the load required to tear the rubber increases with the width of the sample and, therefore, the results should be expressed as kg. per sq. cm. to give a measure of the "true" tear resistance of the rubber.

The A.S.T.M. test-piece is 1 cm. wide and, as a standard nick of .0508 cm. (0.02 inch) is used, either method of expressing the results gives almost the same numerical figure. When varying depths of nick with the A.S.T.M. test-piece are being studied, however, the difference between the two methods becomes greater as the depth of nick increases, the kg. per sq. cm. results being greater than the kg. per cm. results. This is illustrated by Figures 22 and 23, where the two methods of expressing the results are plotted against depth of nick for natural rubber, Neoprene-GN and Butyl treads.

Further interesting evidence to support the view that tear resistance should be expressed as kg. per sq. cm. was obtained when the classical work of Busse<sup>3</sup> was carried out on 1-inch strips of natural rubber tread. These strips were cut to a depth of 0.1, 0.25, 0.50, 0.75, and 0.90 inch, and the tear resistance de-

terminated. The tear resistances calculated as kg. per sq. cm. and as kg. per cm. are plotted against depth of nick in Figure 24. The kg. per sq. cm. curve verifies the results obtained by Busse, and it will be seen that the tear resistance passes through a minimum and then increases. When the width of the un-nicked portion is not considered and the results expressed as kg. per cm. it is seen that the tear resistance falls progressively with the depth of nick. It is, therefore, suggested that, although the same numerical value is obtained approximately with the A.S.T.M., method, whether the results are expressed as kg. per cm. or as kg. per sq. cm., the latter is the more accurate method where the width of the sample is taken into account. This point assumes fundamental significance when the effect of varying the depth of nick is considered and when the width of the sample is varied.

### CONCLUSIONS

(1) Comparative tests have shown the 0.02 in. nick gives the least variable tear resistances for all the rubbers tested. The error of test is higher for synthetic rubbers ( $\pm 22$  per cent for a single test) than for natural rubber ( $\pm 12$  per cent for a single test). These errors of test apply equally at temperatures of  $21^\circ\text{C} \pm 2^\circ\text{C}$ ,  $50^\circ\text{C}$ ,  $70^\circ\text{C}$  and  $100^\circ\text{C}$ .

(2) Adequate data have shown that tear tests are analogous to tensile tests and the width of the sample should be taken into account by expressing the results as kg. per sq. cm. instead of as kg. per cm.

(3) Natural rubber is superior to the synthetic rubbers, but when the depth of nick is increased to 0.20 inch it becomes inferior to Butyl and GR-S.

(4) The results emphasize the poor resistance of the gum stocks of the synthetic rubbers compared with natural rubber, and this difference is accentuated at elevated temperatures.

(5) Experimental results support the theory that higher tear resistance is obtained with rubbers which crystallize on stretching.

(6) The mechanism of tearing is not the same for all rubbers, and it has been found that butyl rubber maintains its tear resistance at elevated temperatures due to the development of knotty tearing. Within a more limited temperature range this effect has also been found to a lesser extent with Noplas-A.

(7) The experimental results have emphasized the need for careful examination of the type of tear developed and also the requirements of accurately analyzing and defining the stress and strain distributions within the sample.

The author is indebted to Miss M. Ogden for carrying out much of the experimental work.

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# MECHANISM OF EXPOSURE-CRACKING OF RUBBERS

## WITH A REVIEW OF THE INFLUENCE OF OZONE \*

R. G. NEWTON

### 1. INTRODUCTION

This investigation has been restricted to the cracking which occurs when stretched rubber is exposed to an outdoor atmosphere, or to ozonized air, and will be called "exposure-cracking". Many earlier authors have called it "sun-cracking", but this is certainly erroneous, as light is not necessary, and may hinder cracking. Van Rossem and Talen<sup>1</sup> used the term "atmosphärischen Rissen", but this is not a convenient description, as the translation "atmospheric cracking" tends to exclude ozonized air. The author believes that these cracks are formed only in the presence of ozone, and he would thus prefer to call the process "ozone-cracking," but such a term might be considered premature, and might be regarded by some readers as excluding outdoor atmospheres.

This type of cracking is characterized by the fissures which form in the surface of rubber at right angles to the direction of stress. There is another type of cracking, which the author prefers to call "crazing", produced on unstretched rubber by light in the presence of oxygen; these cracks may run in any direction, with the result that they readily link up to form a network; they are formed in a resinous skin on the surface instead of in the rubber itself, as is the case with exposure-cracking. Morris, James and Werkenthin<sup>2</sup> give a valuable summary of the differences between cracking and crazing.

These two types of surface deterioration have been much confused in the literature, but it should be noted that exposure-cracking can occur in the dark, whereas crazing does not; crazing can occur also on stretched rubber, so that both types may be present when the latter is exposed to light, in which case their relative magnitudes depend on, among other things, the compounding ingredients employed. This circumstance is probably responsible for some of the confusion in the literature, but several authors, notably Williams<sup>3</sup>, Van Rossem and Talen<sup>1</sup>, Depew<sup>4</sup>, and Morris, James and Werkenthin insist on a distinction between these two types of deterioration.

Several features of exposure-cracking have been little understood, and it has not been generally realized that the causal agencies do not include light, but only strain and ozone, while the reasons advanced to account for the "critical elongation" of rubber at which the cracking appears maximal have not been satisfactory. It is believed that the former has now been adequately demonstrated in Section 4, while an hypothesis has been advanced in Section 5.3.2 to account for the latter. Some attempts have been made in Section 6 to answer the question: "Why does rubber crack at all?", and attention is drawn to the important differences between the concepts: (1) rate of ozone attack; (2) rate of crack-formation; and (3) rate of crack growth. In addition,

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a discussion is provided of methods of assessing the degree of cracking, and the literature is reviewed. The various sections of the paper are self-contained, and each can be read independently of the others, points of overlapping being adequately cross-referred.

## 2. EXPERIMENTAL PROCEDURES

### 2.1 TYPE OF EXPOSURE SAMPLES EMPLOYED

To produce cracking, rubber must be stretched, and the amount of strain is important, especially in the region of 0-50 per cent. Preliminary experiments were carried out on dumb-bells stretched to different extents, but it was soon realized that it would be much more convenient to use a sample with a changing cross-section, so that a continuous gradation of strain was obtained from one end to the other when the sample was stretched. This procedure has several advantages: (1) all values of strain, between certain limits, can be obtained; (2) comparisons of the effects produced by different strains can be made on the same sample, thus reducing the variation due to different samples; (3) a much smaller number of samples is needed to cover a given range of surface strains; and (4) the possibility of different exposure-conditions being encountered at the different strains is much reduced. Van Rossem and Talen<sup>1</sup> were the first to use samples having a progressive change of cross-section, their specimens being produced from a special mould of changing thickness. A more convenient method is described by the R. T. Vanderbilt Co.,<sup>5</sup> where the samples are of uniform thickness but, being a double triangle in plan, the width

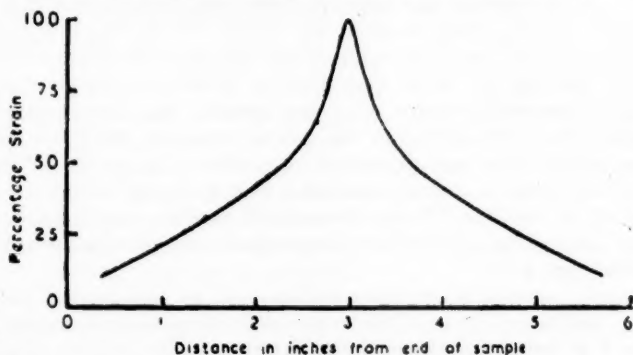
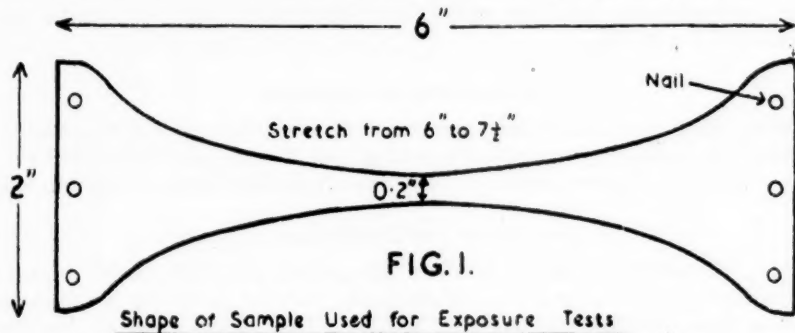


Fig. 2.—Approximate average relationship between strain and position on the sample.

is greatest at the ends. These specimens were used in a few experiments, but they were found difficult to employ with those types of synthetic rubber which have poor tear resistance, because tearing started where the straight edges of the triangles intersected at the narrowest point. Different shapes were then tried, and finally the shape shown in Figure 1 was adopted, because this gave a gradual change of strain in the region of 20 per cent, and yet made it possible to obtain values of 100 per cent. The approximate strain at different points along the length is shown in Figure 2.

For many purposes it is not necessary to know the exact strain at any point, which depends on the stress-strain curve of the vulcanizate, and comparison with Figure 2 is sufficiently accurate. If the actual strain is required, for example, in the region where cracking appears most extensive, a satisfactory method is to make marks on the stretched and cracked surface, and measure the distance separating them, both before and after release. This method is generally to be preferred to marking before exposure because (1) the ink marks may flake or become diffuse on stretching; (2) some kinds of ink and wax-pencil enhance the rate of cracking; (3) the scratches produced by the pen may modify the type of cracking, as noticed by Van Rossem and Talen<sup>1</sup>; and (4) excessive permanent set may give very misleading results, as was noted by Kearsley<sup>6</sup>, who found it advisable to prestretch his samples 72 hours before exposure. The present author prefers to expose at once, as would be the case in service, and allow for stress relaxation by determining the strain after release and recovery. The exposure-specimen shown in Figure 1 could be cut from the usual  $6 \times 6 \times 0.1$ -inch tensile-slab with sharp scissors, or preferably by using a special punch, and was nailed to a board so that the total length was increased to 7.5 inches.

## 2.2. CONDITIONS OF EXPOSURE

When the experiments were commenced it was believed that exposure to sunlight was necessary to produce cracking, but it was later found that this was not essential; further details of these experiments are given in Section 4.2.

## 2.3. EVALUATION OF THE DEGREE OF CRACKING

**2.3.1. Use of graded photographs**—It was noticed that the general appearance of the surface-cracking was closely similar to that occurring in the early stages of flex-cracking; this has also been found by Eccher<sup>6</sup> and by Rainier and Gerke<sup>7</sup>. Some success has already been attained in the R.A.B.R.M. Laboratories in grading flex-cracking by means of standard photographs<sup>8</sup>, and these were therefore used to evaluate the exposure-cracking.

When the photographs were first used to determine the degree of flex-cracking their inter-relationships were not known, and they were therefore lettered, rather than numbered; it was found, however, that the differences between the grades were approximately constant as far as E. When these photographs were used to assess exposure-cracking, it was found, as is shown in Figures 3 and 4, that the differences were still roughly constant and, to facilitate their use for making quantitative comparisons, the photographs A-E<sup>8</sup> were therefore numbered 1-5.

It was found possible to evaluate half-grades, as was done in the case of flex-cracking, and it was also possible to assess gradings more severe than No. 5, photographs F-K being numbered 6-10, but the results are less reliable than gradings 1-5.

The justification for numbering the photographs, rather than lettering them as was done previously, is shown in Figures 3 and 4. In Figure 3 the grading of the severity of the cracking produced in the stretched rubber has been plotted against the period of exposure, smooth curved lines, lying through the points, being obtained, showing that the observer was successful in grading the cracking accurately. In the case of flex-cracking it was found that the degree of cracking was linearly related to the logarithm of the period of running of the machine.<sup>9</sup> Similarly, Figure 4 shows that the degree of exposure-

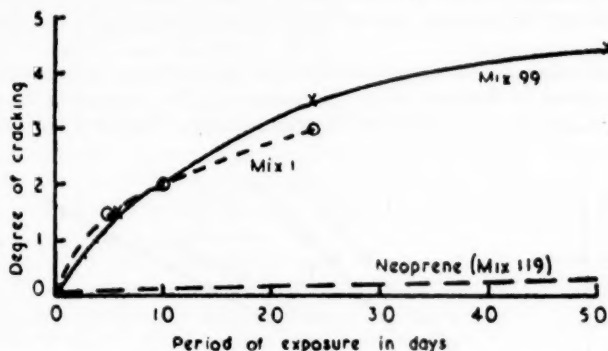


Fig. 3.—Change of degree of cracking with period of exposure.

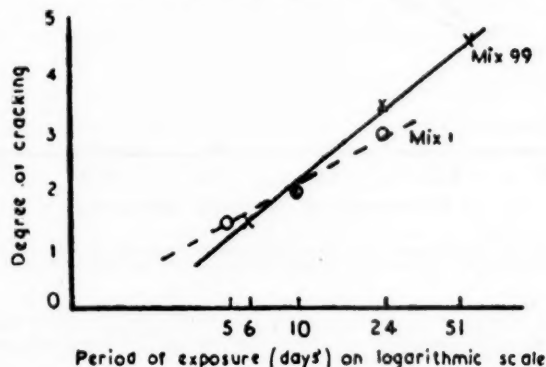


Fig. 4.—Relation between degree of cracking and logarithm of period of exposure.

cracking is linearly related to the logarithm of the period of exposure. This linear relation suggests that the data would be amenable to discriminant function analysis, as was done for flex-cracking by Newton<sup>8</sup> and Stevens<sup>9</sup>; this has not been done, as it is clear that the problem will be complicated by the different behavior at different strains (see Figures 6a-6f).

**2.3.2. Microscopic evaluation of cracking**—It was found that, in ceratin circumstances, a useful method of evaluating the degree of cracking depended on the use of a microscope (magnification up to 300 diameters). For example, by using a transparent vulcanizate, and observing the appearance of the first cracks under the microscope (these initial cracks are about  $1\mu$  long, i.e., about  $1/20,000$  inch), it was found that cracking could be detected after only 2 hours'

exposure out-of-doors. In this way it proved easy to assess the cracking occurring on any one day, and thus to correlate the deterioration with changes in the weather, for example, on very foggy days no cracking occurred at all (these results are discussed more fully in Section 4.5.4).

Microscopic observation of cracking proved particularly valuable in the study of the rate of growth of cracks; while some cracks grow, others diminish in size, see Section 5.1.2. Among earlier authors, Van Rossem and Talen<sup>1</sup> and Norton<sup>10</sup> observed the cracks under a microscope, while the former pointed out the advantages of using transparent vulcanizates. The relationships between the results of grading and of microscopic observation are discussed in Section 5.4.

**2.3.3. Evaluation by changes in mechanical properties**—Several authors followed the progress of deterioration by measuring the concomitant changes in mechanical properties, and Werkenthin, Richardson, Thornley and Morris<sup>11</sup>, in

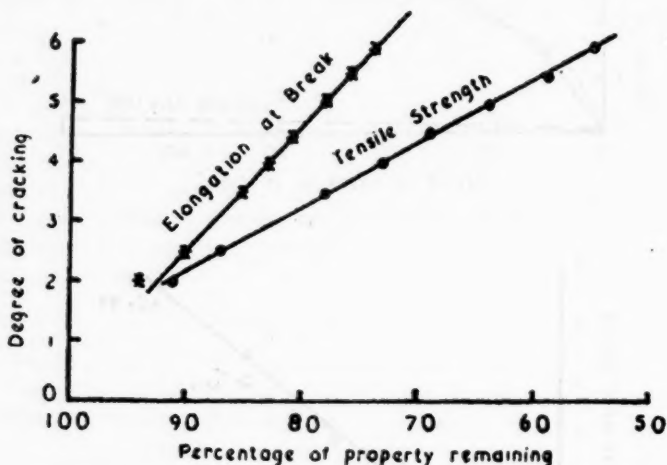


Fig. 5.—Relation between the tensile strength or elongation at break, and the degree of cracking, resulting from exposure of the dumb-bell.

summarizing the literature, believed that it would be an advantage to follow the decrease in tensile strength, or the lowering of the percentage elongation at break.

As a method of studying exposure-cracking this method has several disadvantages, for example, although Werkenthin find, for their type of sample, that the change in physical properties is a more satisfactory means of judging the deterioration than is the appearance of the exposed surface, it is clearly important to distinguish between the total deterioration, and that, due to surface-cracking, the relation between these being influenced by the thickness of the sample. Dawson and Scott<sup>12</sup> exposed squares of rubber, some folded and some unfolded, the former developing surface-cracking at the folds, while the latter did not, yet they failed to distinguish between the two by means of tensile tests on Schopper rings cut from the sheets.

The present author followed these tensile and elongation changes during the exposure-cracking of a GR-S tire-tread vulcanizate, and the results are illustrated in Figure 5, where the tensile strength and elongation at break

remaining after exposure are expressed as percentages of the value before exposure, and plotted against the degree of cracking as graded by the method described in Section 2.3.1. The points shown in Figure 5 were taken from smoothed curves for tensile strength, elongation at break, and grading, plotted against period of exposure. The changes in properties are smoothly related to the changes in the degree of cracking, and the points lie well on the lines (the total period of exposure was only 21 days, and hence it was not likely that much deterioration occurred in the body of the rubber).

It is not clear why the straight lines in Figure 5 would intersect the ordinate at a degree of cracking corresponding approximately to grade 1. Actual dumb-bells were exposed in a bent state, instead of cutting them from an exposed sheet, and it was noticed that the cracks at the edge of the test-length were appreciably deeper than those in the surface, and the degree of cracking was, therefore, probably rated too high. Further work on these lines was not carried out because the visual grading was found to be so much quicker and easier than the performance of tensile tests, while the latter possessed no marked advantages from the point of view of assessing cracking, and moreover would not provide information about the influence of different strains, as does the single sample of the type shown in Figure 1. Another marked advantage of grading the samples lies in the nondestructive nature of the test, the same sample being followed for a period of time, as in Figures 13, 14, and 16.

The author would agree, however, that light produces changes in the sample while ozone is producing cracking, and that the best method of detecting the former might well be by means of tensile tests; for example, Garvey and Emmett<sup>14</sup> found that a Perbunan sample could show a marked decrease in tensile strength without any evident surface-deterioration.

### 3. PRELIMINARY EXPERIMENTS

These results were obtained during an extensive examination of the exposure cracking behavior of different rubbers, and of the influence of changes in the compounding ingredients; certain of the results have been selected as having a bearing on the mechanism of exposure-cracking; all the data are set out together in this section, while the fuller discussion will be postponed until later sections, as indicated. The compositions of the mixings are given in the Appendix.

#### 3.1. INFLUENCE OF STRAIN ON THE DEGREE OF CRACKING

Exposure samples shaped as in Figure 1 are particularly convenient for examining the relation between the strain in the surface, and the degree of cracking produced. Figures 6a-6h show the relationship between strain and degree of cracking for different rubbers after different periods of exposure out-of-doors, or to ozonized oxygen containing  $1.0 \times 10^{-3}$  cc. per cc. of ozone.

In the case of natural rubber, and the polymers and copolymers of butadiene (Figures 6a-6f), there is a well-marked "critical strain" at which the degree of cracking is much more severe than at higher or lower values of the strain, but which tends to decrease slightly, and become somewhat less well-defined, as deterioration proceeds. In all these cases the "critical strain" is at a similar elongation, and the behavior is generally similar, any differences being only relatively small; for example, the critical strain appears to be slightly better defined in GR-S (Figure 6c) than in Hycar-EP (Figure 6d).

On the other hand, the Neoprenes and Thiokol-FA (Figures 6g-6h) show

quite different phenomena; there is no apparent critical strain, and the degree of cracking increases uniformly up to the highest strains examined (this is discussed in Section 5.3.3). These synthetic rubbers are much more resistant to exposure-cracking (Figure 6g) and to the ozonized oxygen used (Figure 6h), natural rubber being cracked right through 0.1-inch thickness in 7 minutes by the latter; note the long periods of exposure in Figure 6g, and the very small values reached by the Neoprene vulcanizate shown in Figure 3 (Mix 119).

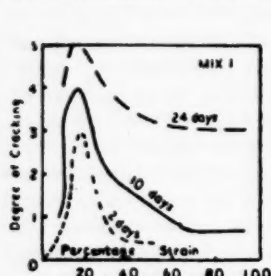


Fig. 6a. NATURAL RUBBER

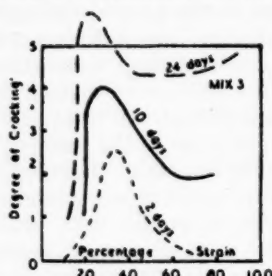


Fig. 6b. POLYBUTADIENE

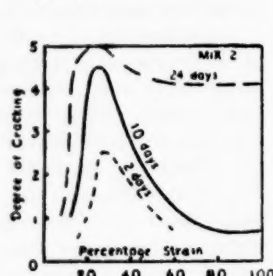


Fig. 6c. GR-S

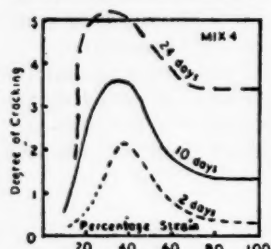


Fig. 6d. HYCAR EP

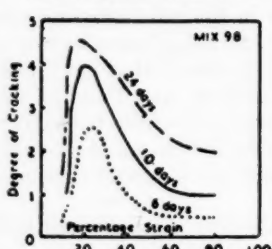


Fig. 6e. PERBUNAN

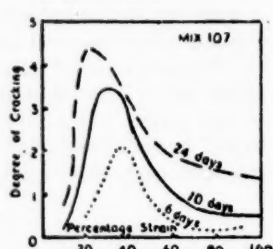


Fig. 6f. HYCAR OR-15

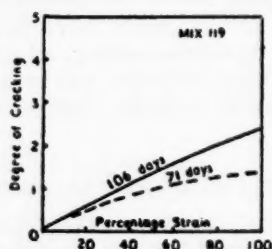


Fig. 6g. NEOPRENE GN

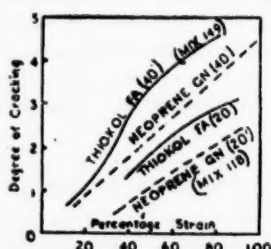


Fig. 6h. AFTER EXPOSURE TO OZONISED OXYGEN FOR 20 AND 40 MINUTES

Small modifications in compounding ingredients may have a profound effect on the relation between strain and degree of cracking. Figure 7a shows the strain-cracking curves for four mixings containing different proportions of paraffin wax. Mix 170 is a GR-S tire-tread type mixing, while Mixings 172-174 contained, in addition, 1, 2, and 5 parts, respectively, of paraffin wax. The addition of 1 part of paraffin wax does not inhibit cracking, although the maximum occurs at a slightly higher strain. When two parts of paraffin wax are employed, the relationship is changed entirely, although there is little change in the maximum cracking, but the use of 5 parts of wax ensures considerable protection. A number of softeners, extenders, and even inorganic materials

have a similar effect on the strain-cracking relationship. On the other hand, some waxes behave quite differently, as is shown in Figure 7b, for 5 parts of carnauba wax in the same base mixing. The effects shown in Figures 7a and 7b are explained in Section 5.3.3.

### 3.2. INFLUENCE OF STRESS ON THE DEGREE OF CRACKING

Some authors have claimed that a "critical stress" is more characteristic of rubbers in general than is a "critical strain". Haushalter, Jones, and Schade<sup>15</sup> say "the maximum cracking takes place more nearly at a definite tension than at a definite elongation" and they find, for four different natural rubber compounds, that the elongation at which the maximum loss of tensile strength occurs during exposure ranges between 5 and 12 per cent, whereas the corresponding stress figures lie between 0.8 and 1.4 kg. per sq. cm. (11–20 lb. per sq. in.). On the other hand, Haushalter himself<sup>16</sup> found that the degree of cracking was more severe at a tension of 40 lbs. per sq. in. than at 20 lbs. per sq. in. Ball, Youmans, and Rausell<sup>17</sup> tested two compounds and found the

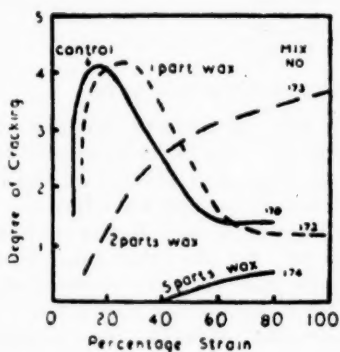


FIG. 7a.—Relation between strain and degree of cracking for mixings containing different proportions of paraffin wax, after 10 days' exposure.

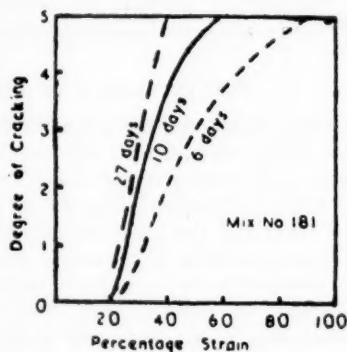


FIG. 7b.—Relation between strain and degree of cracking for a mixing containing 5 parts of carnauba wax.

maximum cracking at strains of 15 and 50 per cent, respectively, both these strains being equivalent to a modulus of 75 lbs. per sq. in. When these data are compared with one another, it appears that, for rubbers in general, neither the "critical strain" nor the "critical stress" is particularly constant. Some further information on this question can be obtained from Figures 6 and 7, as the stress-strain curves of the rubbers are known; the critical strains range between 19 and (say) 100 per cent, while the corresponding stresses lie between 40 and 200 lbs. per sq. in.

### 3.3. INFLUENCE OF THE DIFFERENT RUBBERS

From the point of view of the maximum cracking occurring after 10 days' exposure there is little difference between the rubbers shown in Figures 6a–6d, although more extensive work has indicated that GR-S is definitely less resistant than is natural rubber, and the order (from best to worst) is probably: natural rubber, GR-S, polybutadiene, Hycar-EP (the 2-day figure for Hycar-EP is unduly low). There is, thus, no clear relation between the resistance to

cracking and the amount of butadiene replaced by styrene in the copolymers, although the change from butadiene to methylbutadiene (isoprene) in the simple polymer leads to an improvement in resistance; this may, however, be due to the change from an irregular to a regular polymer. On the other hand, the partial replacement of butadiene by acrylonitrile in the copolymers leads to a distinct improvement, the degree of resistance increasing in the series 6b, 6e, 6f, as the acrylonitrile content increases.

The change from butadiene to chlorbutadiene (Figures 6b and 6g) produces a large increase in resistance to exposure-cracking, and it is clear that there is some important difference between the Neoprenes and Thiokol-FA on the one hand (Figure 6h), and the butadiene and isoprene rubbers on the other; this difference is discussed more fully in Section 6.3. In Figure 6h the samples were exposed to ozonized oxygen containing  $1.0 \times 10^{-3}$  cc. per cc. of ozone; this concentration will crack an unprotected natural-rubber sample 0.1 inch thick right through in seven minutes, and it is evident that these synthetic rubbers are very highly resistant.

It is intended to carry out further tests on Neoprene types, using "pure-gum" vulcanizates, so that the nature of the cracking can be compared with that found in the butadiene and isoprene types.

#### 3.4. INFLUENCE OF COMPOUNDING INGREDIENTS

Certain compounding ingredients in the vulcanizate produce marked changes in the resistance to exposure-cracking. The effects produced by paraffin wax and carnauba wax have been illustrated in Figures 7a and 7b, the former being protective while the latter appears actually to reduce the resistance to cracking; the proprietary waxes Okerin-333 and Heliozone have this protective propensity particularly prominent. On the other hand, five parts of wool grease fat-acid or chlorinated naphthalene wax have no effect on either the resistance to cracking or the value of the critical strain, and it thus appears that materials with apparently similar physical properties may produce one of the three kinds of effect on the resistance to exposure-cracking.

Another well-marked effect is found when white fillers, such as magnesium carbonate or whiting, are employed. When vulcanizates containing these fillers are exposed out-of-doors, cracking does not develop at first, but a resinous skin forms on the surface of the rubber, the presence of the skin being easily demonstrated by the wrinkled effect produced when the thumb-nail is pressed into the surface. After a further period of exposure, this resinous skin crazes and permits ozone to pass down the resultant fine cracks and attack the rubber; further skin formation seems not to occur at the bottom of the crack, and this may be due to reduced light density below the skin. This cracking frequently occurs earliest at the highest strains (about 100 per cent elongation) and the anomalous effect is produced of the rubber having apparently a great resistance to exposure-cracking, yet suddenly breaking right through at high elongations. The explanation of these phenomena is given in Sections 4.6.1 and 5.3.3.

This effect of white fillers is found with natural rubber and different synthetic rubbers, and is particularly well marked when French chalk, colloidal china clay, or activated whiting is used as the filler. The data in Table I illustrate the effects found, the degree of cracking shown in the table being the maximum found, irrespective of strain, in the region of 10-100 per cent strain. The apparent protection by white fillers is destroyed by even a small proportion of carbon black, as is shown by Mixings 86 and 87; the reasons for the ap-

parently adverse effect of carbon black, and the beneficial effect of magnesium carbonate (see Mixings 101 and 110), are given in Section 4.6.1.

Some of the data in Table I are plotted in Figure 8, which is similar to Figure 3, to illustrate the marked difference in behavior which is found with these white fillers.

TABLE I  
INFLUENCE OF WHITE FILLERS

Mix No.	Description of vulcanizate		Maximum degree of cracking after period of exposure (days) stated			
	Elastomer	Filler	6	10	24	51
52	GR-S	Activated whiting, 105	0	$\frac{1}{2}$	6	*
53		Silene, 91	0	0	$1\frac{1}{2}$	4
54		CCC, 105	0	0	6	*
86		Activated whiting, 70; Silene, 30	0	$\frac{1}{2}$	2	?
87		Ditto, + MPC, 5	3	5	8	*
101	Perbunan	Magnesium carbonate, 65	0	$\frac{1}{2}$	2	2
103		French chalk, 80	0	2	8	9
110	Hycar OR-15	Magnesium carbonate, 65	0	0	1	3
111		CCC, 80	0	1	6	7
112		French chalk, 80	0	$\frac{1}{2}$	5	7

The amounts of fillers, given in the table, indicate the number of parts by weight of filler per 100 parts of the elastomer, the abbreviations being: CCC, colloidal china clay; MPC, medium-processing channel black. An asterisk (\*) indicates that the sample broke.

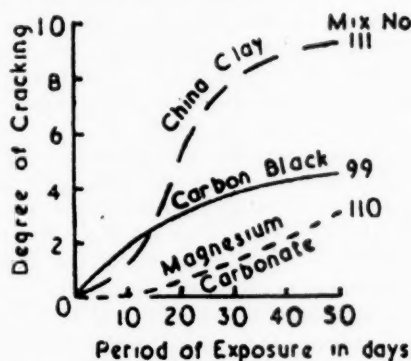


FIG. 8.—Influence of fillers on exposure cracking.

#### 4. AGENCIES RESPONSIBLE FOR EXPOSURE-CRACKING

##### 4.1. SUMMARIZED CONCLUSIONS

It is shown that the only factors essential for exposure-cracking are ozone and strain in the sample, and that sufficient ozone is present in the atmosphere to produce the deterioration observed. Light is shown not only to be unnecessary, but actually to have a retarding effect on the production of cracks; the term "sun-cracking" is therefore quite erroneous. Arguments are advanced against the speculations of Dufraisse<sup>18</sup> that dust is responsible for cracking. Temperature changes may affect the rate of cracking in ways which depend on the type of mixing used, while changes in oxygen and humidity do not influence the rate of cracking.

## 4.2. PRELIMINARY EXPERIMENTS

Exposure-cracking is so frequently referred to as "sun-cracking" that the first experiments were planned to determine whether light is actually an essential factor in producing these cracks. Tire-tread and transparent natural-rubber vulcanizates were used in this work, the initial samples being shaped as in Figure 1, while subsequently strips of the transparent vulcanizate, stretched 60 per cent, were used, because it was found that the onset of cracking could be detected most easily by this means (see Section 5.1). The samples were nailed, in the stretched condition, to pieces of wood. These initial experiments can be placed in four categories.

(1) Samples exposed in stoppered glass bottles, glass tubes, quartz tubes, and a closed brass box with a quartz lid, showed no cracking at all, after a period of six weeks' exposure on the roof, facing the sun.

(2) When the glass bottle was unstoppered, and if baffles were arranged at the ends of the glass and quartz tubes so that fresh air could circulate, but unfiltered light could not enter through the ends, or if fresh air was sucked through holes made in the brass box, cracking occurred in a few days. Hence light cannot itself produce cracking in stretched rubber, and some component of the air is essential. Similarly, Williams<sup>3</sup> noted that stretched samples exposed in "a well-ventilated glass box" cracked readily, but "if the box was sealed so that air currents could not enter, skin formation resulted, but no cracks appeared".

(3) Samples in complete darkness, inside metal tubes, cracked severely if fresh air were drawn through from outside the building, but not, or only relatively slowly, if the air was drawn from the laboratory. Hence light is certainly not necessary, and the active agency is not always present in the air. In an experiment in which stretched samples were exposed to air drawn from the laboratory, Van Rossem and Talen<sup>1</sup> found that no cracking occurred over a period of a month.

(4) On the other hand, some samples were exposed in complete darkness in a cardboard box, through which air could circulate, but light could not enter. These samples did not show any cracking until the box commenced to disintegrate from exposure to the weather. The result of this experiment proved puzzling until an observation by R. H. Norman, of the R.A.B.R.M., provided a clue; during some experiments with stretched rubber exposed to ozonized oxygen, he noticed that cracking occurred only on the top-side of the specimen, and not on the under-side in contact with the pine-wood support. When a piece of glass was placed between the stretched rubber and the wood, cracking occurred on both sides, and it thus appeared that the wood absorbed the ozone before it could attack the rubber.

If ozone is responsible for normal exposure-cracking of rubber, it is now understandable that experiment (4) should fail, because the cardboard baffles would probably have removed the ozone from the air before it reached the rubber; Ewell<sup>59</sup> showed that an untreated cardboard box absorbed ozone readily. Similarly, in experiment (1), the stoppered vessels would soon be free of ozone, due to absorption by the wood on which the sample was supported, even if enough had been present to produce cracks on the rubber. Thus, suspicion should be placed on conclusions about the influence of excluding light, if the light is prevented from entering by means of organic materials, *e.g.*, by placing the samples in a wooden drawer. Thus, Tener, Smith, and Holt<sup>19</sup> conclude that cracking does not occur in the absence of sunlight, but they excluded the

light by using a box with black cloth over the ends, and thus vitiated their conclusions. Asano<sup>20</sup> concluded that cracking is produced by ultraviolet light, but his sample which did not crack was "covered with a piece of thick black paper for the purpose of protection from light", thus removing ozone as well, through absorption by the paper.

Reynolds<sup>21</sup> sucked air through glass tubes containing stretched rubber samples, and found that no change in the rate of cracking was produced by excluding light from the tubes; he showed also that the ozone content of laboratory air is diminished, largely by the whitewash on the ceiling (see Section 4.5.3, for further details). Various other workers noted that cracking was less severe in laboratory air, but attributed the change to the lower light intensity; actually "fresh air", which has not had the ozone removed, appears to be necessary.

Williams<sup>3</sup> concluded that light was not essential, as his sample cracked equally, if not more readily, on the unexposed side, while Van Rossem and Talen<sup>1</sup> demonstrated that samples which were exposed only at night cracked quite normally, and Potter<sup>22</sup> found the same result. The present author repeated this experiment at the September equinox, one sample being exposed only at night, and the other only by day, the samples being kept in a closed box when not exposed; after a week, both samples had cracked equally.

### 4.3 SUBSEQUENT EXPERIMENTS

Reynolds<sup>21</sup>, when using the tubes referred to above, found that cracking could be prevented by first filtering the air with either copper sulfate crystals or chalk, either of which is claimed catalytically to decompose ozone. The present author has carried out similar experiments in which the air was filtered by various reagents; the experiments were carried out in complete darkness to avoid the disturbing effect produced by the oxidized skin formed on rubber by the action of light, which, as noted by Williams<sup>3</sup> and Van Rossem and Talen<sup>1</sup>, tends to reduce the extent of cracking (see also Section 5.3.3).

An air-tight metal tube, containing the sample, was placed on a window-sill outside, and near the top of, the building, outside air being sucked through the tube at about 0.3 liter per minute. When the incoming air was unfiltered it was often possible to detect the onset of cracking in 2 hours, but the day-to-day variations in rate of cracking made it essential to run a control sample, in a second tube, at the same time. Filters of sawdust or glass wool inserted in the incoming air stream completely prevented cracking; the former absorbs ozone and the latter produces catalytic decomposition of the gas; the glasswool, however, was not completely effective when the rate of flow of air was increased to 1 liter per minute. Pure cotton wool is said not to decompose ozone,<sup>23</sup> but a filter composed of this material prevented cracking. It was, however, noticed that a considerable amount of dust was filtered from the air, and this may well itself have acted as the filter and decomposed ozone, forced into closer proximity with the dust than would have been the case in the atmosphere (see Section 4.5.3). This presence of dust in the air will be referred to again in Section 4.4, and it may invalidate the conclusions referred to above for finely divided filters.

In view of the difficulty experienced with filters composed of finely divided solids, which trap dust and thereby become impure, further experiments were carried out with solutions. When an acidified 0.01 *N* potassium permanganate solution was used, the solution was partly decolorized after 24 hours, but the degree of cracking in the experimental tube was equal to that in the control. According to Keiser and McMaster<sup>24</sup> this reagent should destroy hydrogen

peroxide and nitrogen peroxide, but leave the ozone untouched; it appears likely that it also removed some of the dust from the air, which partly decolorized the solution. When 10 per cent chromic acid solution was used, some cracking occurred in the experimental tube, but certainly less than in the control tube. According to Usher and Rao<sup>25</sup> this reagent should destroy hydrogen peroxide, but leave ozone and nitrogen peroxide unaffected; Bamberger and Trautzl<sup>26</sup> point out also that chromic oxide and potassium permanganate do not decompose ozone. The results of this experiment are not conclusive, but it is likely that the organic matter in the air was decomposed by the chromic acid, and it is possible that some of the end-products decomposed part of the ozone, thus reducing the cracking.

Van Rossem and Talen<sup>1</sup> did not prove conclusively that ozone is the causative agency, but they pointed out that the cracking phenomena were exactly similar in both "atmospheric-cracking" and ozone attack, that other chemically reactive gases which might be present in the atmosphere (oxides of nitrogen, sulfur dioxide, and chlorine) did not produce cracking, and that it was not improbable that the ozone concentration of the surface air was higher on windy days, while they observed the cracking to be worse on such days. This last question is discussed in Section 4.5.

#### 4.4. COMMENTS ON THE "ACTIVATED DUST" THEORY OF DUFRAISSE

In the author's opinion, only one hypothesis about the causative agency in the atmosphere seriously challenges the contention that ozone is responsible for exposure-cracking, *i.e.*, that advanced by Dufraisse<sup>18</sup>. He points out that particles of organic matter in the air may show the Russell effect when irradiated by sunlight, and thus contain relatively volatile reactive organic peroxides which may remain stable for some hours. He suggests that when these settle on a stretched rubber surface they will cause a peroxidic attack possibly similar to that procured by ozone. If the reactivity were to persist for some hours, the particles could cause cracking at night and, in fact, they might be generally indistinguishable from ozone. In view of the decomposition of ozone by dust collecting in the filters, it may well prove difficult to distinguish between these activated particles and ozone, unless the exposure experiments are carried out in the stratosphere. However, the author advances the following suggestions for rejecting the theory.

(1) Van Rossem and Hessels<sup>27</sup> showed that the Russell effect can be produced in raw rubber (smoked sheet) by exposing it in a sealed box with a glass lid. If the organic particles behaved like smoked sheet, they should continue to be re-activated in the stoppered glass containers (see Section 4.2, experiment (a)), or at least in those composed of quartz, which is transparent to all the ultraviolet radiation present in sunlight at the surface of the earth.

(2) Cracking should be produced on sunny and hazy days when there is no wind, and hence no ozone is present; Reynolds<sup>21</sup> showed that no exposure-cracking occurs on such days (see Section 4.5.4.)

(3) From a chemical point of view, these organic peroxides might be expected to behave like hydrogen peroxide, to discolor potassium permanganate solution, and be removed by chromic acid; both of these reagents might therefore be expected to prevent "dust-cracking", but the former does not prevent exposure-cracking, while the latter only reduces the extent.

(4) Following the argument in (3), peroxides might be expected to produce

cracking, but various experiments with different concentrations of hydrogen peroxide, and one with acetone peroxide, all failed to produce any cracking.

(5) During microscopic observation of the cracks, particles of dust are frequently seen on the rubber surface, and some lodge on the rubber so permanently that they remain until the end of the experiment. If such particles are the cause of cracking, the cracks should radiate from the particles, but this has never been seen; an example of dust on the surface, and its failure to modify the course of cracking is shown in Figure 10b.

(6) Commercial calcium chloride will prevent exposure-cracking in air which has been passed over it, but if the material has been carbonated by passing carbon dioxide through it and thus removing the alkali which destroyed the ozone, cracking readily occurs. It would appear unlikely that this change in the calcium chloride would alter the ease with which dust passed through the filter.

#### 4.5. PROPERTIES OF OZONE AND ITS AVAILABILITY IN THE ATMOSPHERE

Other hypotheses about the active agency in producing exposure-cracking have been advanced by various workers; the author's criticism of these will be mainly from the point of view of experimental technique or interpretation of the results, the earlier workers having failed to realize how little ozone is required, or how easily it is decomposed. For this reason it will be useful first to consider the amounts of ozone available in the atmosphere, and some of the properties of this oxidizing gas.

4.5.1. *Ozone content of the atmosphere*—Some authors, *e.g.*, Duclaux<sup>28</sup>, Merz<sup>29</sup>, and Edgar and Paneth<sup>30</sup>, have argued that ozone does not exist in the atmosphere, or at least that the amount is insufficient to produce the degree of exposure-cracking found. On the other hand, several authors regard the ozone content as adequate for this purpose and, in particular, Van Rossem and Talen<sup>1</sup> explained the factors controlling the ozone content so lucidly that subsequent advances in knowledge add relatively little to their account. In view of these conflicting reports, it will be useful to summarize the present position.

Ozone is produced in the stratosphere by the action, on oxygen, of the extreme ultraviolet components of sunlight; it diffuses to the troposphere<sup>31</sup>, and winds bring it down to the surface of the earth<sup>32</sup>, where it is decomposed by organic matter and by reducing gases, especially sulfur dioxide, produced by burning coal in towns. Certain aspects of this chain of phenomena deserve fuller consideration, and are discussed in the following sections.

4.5.2. *Rate of transfer of ozone from the stratosphere*—There is a considerable gradient of ozone concentration with altitude, Dobson<sup>33</sup> having estimated the concentration at a height of 20 km. as  $10\text{--}15 \times 10^{-8}$  cc. per cc., while the mean concentration at ground level was  $4 \times 10^{-8}$  cc. per cc. The theory that wind is responsible for transfer of ozone through the troposphere was first advanced in 1869, and this concept has received considerable support from many authors; for example, Gluckauf and Paneth<sup>34</sup> found that the ozone concentration of the air at Durham depended on the intensity and direction of local winds, those blowing from the direction of the city (north) never containing any ozone, while west winds exceeding 5 m.p.h. nearly always contained ozone, the amount sometimes being as high as  $3.6 \times 10^{-8}$  cc. per cc.; stagnant air contained no ozone (less than  $0.1 \times 10^{-8}$  cc. per cc.).

It has been shown also that depressions and anticyclones have an important

bearing on the concentration of surface ozone, for example, Dobson<sup>36</sup> recorded large changes of ozone concentration (of the order of 25 per cent) within a few days, the concentration being high around a cyclonic depression, especially just to the west of the center of low pressure, while the amounts of ozone were always below normal around a high pressure area. Tonsberg and Chalonge<sup>36</sup> comment on the same phenomenon, and Gluckauf<sup>37</sup> showed that variations in the ozone content of surface air are very marked, the annual maximum value, in May, being  $6.8 \times 10^{-8}$  cc. per cc., while the highest value in November was only  $2.4 \times 10^{-8}$  cc. per cc. (These variations are greater than the corresponding one for ozone in the stratosphere, probably due to the greater instability of the atmosphere in spring and to more coal smoke in the winter.) Meetham<sup>31</sup> explained the efficiency of a depression in increasing the ozone content of surface air by postulating a lowering of the tropopause at this point, and Gluckauf<sup>37</sup> related the local variations to the structure of the depression. Wulf<sup>38</sup> summarizes the knowledge of the different steps in the process.

4.5.3. *Fate of the surface ozone*—A balance is maintained between the rate of transfer of ozone from the stratosphere, and its rate of destruction either by oxidizable materials or by catalytic decomposition. In the surface air the ozone is reduced by organic dust and by sulfur dioxide, or is decomposed by nitrogen peroxide<sup>21</sup>; in contact with the ground it is reduced by organic matter, while in buildings it is reduced by wooden fittings and is catalytically decomposed by calcium carbonate (especially whitening on the ceiling) and by metallic oxides<sup>21</sup>. Heavy and continuous rain stabilizes the ozone content by washing sulfur dioxide and nitrogen peroxide from the air, and Reynolds<sup>39</sup> recorded a marked increase in ozone content during an extensive thunderstorm, although there is no proof that any ozone is produced by lightning discharges. Foggy or sultry conditions result in the total disappearance of ozone<sup>40</sup>, due to the failure of winds either to renew the supply to, or remove the products of combustion from, the locality.

4.5.4. *Correlation between ozone content of the atmosphere and cracking of rubber*—Reynolds<sup>21</sup> and Van Rossem and Talen<sup>1</sup> both found that stretched rubber cracked more rapidly during windy days, and the former found no cracking during sultry weather conditions, while he also recorded that the rate of cracking increased with altitude in the Swiss mountains; all these changes are in qualitative agreement with the changes in ozone content under similar conditions. McKee and Depew<sup>41</sup> found the cracking to be worse on "hazy" days, and attributed the effect to humidity, but this has not been the author's experience, and the observation is not understood.

The author found that his strips of transparent rubber would show microscopic cracks in a few hours on some days, and a 24-hour record (five days per week) of the degree of cracking was kept; considerable differences in rate of cracking were found on different days, and no cracking at all occurred on some foggy days. The mean of five windy days (Beaufort Scale 3 and higher) gave a rate of cracking 14 times higher than that for the mean of five foggy days. It is intended to set up an apparatus similar to that used by Gluckauf, Heal, Martin and Paneth<sup>42</sup>, but without the automatic pipette and associated electrical equipment, so as to correlate the changes in rate of cracking with daily changes in the ozone content of the atmosphere.

4.5.5. *Adequacy of the ozone concentration of the atmosphere for producing the extent of cracking observed*—Various authors have worked with ozonized air and thus accelerated the rate of cracking; from their data an estimate can be made of the rate of cracking in atmospheric air. The data given by Norton<sup>10</sup>

show that, at certain stresses and over certain concentrations, the period required to crack a sample right through is inversely proportional to the ozone concentration. This suggests that the product of concentration and time ( $c \times t$ , where  $c$  is in cc. per cc., and  $t$  is in minutes) should be approximately constant. The validity of this suggestion can be examined by using the data from those workers who employed ozonized air and also recorded the times and concentrations used. Their findings are summarized in the table below.

Authors	$t$	$c$ (cc. per cc.)	$c \times t$ ( $\times 10^{-3}$ )
Ball, Youmans, and Rausell <sup>17</sup>	30 min.	$1.4 \times 10^{-4}$	4
Eccher <sup>6</sup>	15-50 hr.	$1 \times 10^{-6}$	0.9-3.0
Haushalter, Jones, and Schade <sup>18</sup>	1 min.	$1 \times 10^{-3}$	1
Kearsley <sup>43</sup>	30 min.	$2 \times 10^{-5}$	0.6
Potter <sup>22</sup>	15 min.	$1.5 \times 10^{-4}$	2

Thus, these values range between  $0.6 \times 10^{-3}$  and  $4 \times 10^{-3}$ , i.e., the value is surprisingly constant in view of the different concentrations employed, the different extents to which the attack was carried, the different vulcanizates and the different strains used.

Still other data are available on this point: Van Rossem and Talen<sup>1</sup> found that the first cracks developed after five minutes' exposure to a concentration of  $3 \times 10^{-5}$  cc. per cc., ( $c \times t = 0.2 \times 10^{-3}$ ), the value certainly being low because only the first cracks were observed. They remark also that 30 minutes' exposure is equivalent to one week in the normal atmosphere. Norton<sup>10</sup> employed widely varying concentrations and stresses, and his test was also unusual, the time recorded being that required to break a thin rubber strip, extended under constant load; representative extreme examples are: 4 minutes at  $5 \times 10^{-5}$  cc. per cc., and 3 seconds at  $5 \times 10^{-2}$  cc. per cc. ( $c \times t = 0.2 \times 10^{-3} - 2.5 \times 10^{-3}$ ); Williams<sup>3</sup> noted that the ozone concentration had to be reduced to  $2 \times 10^{-5}$  cc. per cc., for the cracking to be slow enough to enable accurate observations to be made.

The A.S.T.M.<sup>44</sup> recommended an exposure of one hour at  $1.0 \times 10^{-4} - 1.5 \times 10^{-4}$  cc. per cc., for testing ozone-resistant cables ( $c \times t = 6-9 \times 10^{-3}$ ), while Baggish and Meade<sup>45</sup>, for the same purpose, advocate 3 hours at  $8 \times 10^{-5}$  cc. per cc. ( $c \times t = 14 \times 10^{-3}$ ); these exposures are probably rather severe in view of their purpose. Similarly, Haushalter<sup>16</sup> cracked his samples completely through in  $1\frac{3}{4}$  minutes at  $5 \times 10^{-3}$  cc. per cc. ( $c \times t = 9 \times 10^{-3}$ ), and the exposure is again excessive. Kearsley<sup>43</sup> noted that the nature of the cracking was independent of the ozone concentration.

Thus the extreme range of values for the product ( $c \times t$ ) is (1)  $0.2 - 14 \times 10^{-3}$  while normal values (2) lie between 0.6 and  $4 \times 10^{-3}$ . If the normal concentration of ozone in the atmosphere is taken as  $4 \times 10^{-8}$  cc. per cc., these ranges would be equivalent to (1) 3-240 days, or (2) 10-70 days. In actual practice, cracking can usually be detected by the naked eye in 2 days, and is often moderately extensive in 7 days, so that either (1) ozone becomes relatively more efficient in great dilution; (2) some other agency also produces exposure-cracking; or (3) those workers who used ozone probably produced deeper and more extensive cracking than that regarded as severe when the much slower atmospheric exposures have to be considered; the present author's experience is that the use of ozonized air, with its rapid rate of attack, tempts the experimenter to be really severe with the sample.

To determine the relative importance of the factors (1-3), given above, it is intended to carry out some experiments with low concentrations of ozonized

air. To produce very low concentrations it is hoped that a diffusion method can be employed, the concentration of ozone being controlled by diffusion through a membrane.

#### 4.6. OTHER FACTORS CLAIMED TO CAUSE EXPOSURE-CRACKING

The strain in the surface of the rubber is the other main factor in causing exposure-cracking, and it will be considered fully in Section 5.

4.6.1. *Light*—Many authors have believed that light is the main factor in exposure-cracking, and this has led to the phenomenon becoming known incorrectly as "sun-cracking", for example, Jackson<sup>46</sup>, as the result of making a survey of the literature in 1934, was convinced that light was the causal factor. This false belief has arisen as the result of two types of experiment: on the one hand, workers wishing to study the behavior of samples in the absence of light have placed them in wooden drawers, covered them with cloth, or otherwise prevented ozone from reaching them (see remarks in Section 4.2). On the other hand, several workers have noticed that effective cracking is produced when samples are exposed out-of-doors, while far less cracking is produced indoors, as reported by McKee and Depew<sup>47</sup> and Evans<sup>48</sup>, or when artificial illumination is used, and they have concluded that the quality of the light is unsatisfactory under these conditions, although the real reason lies in the low ozone content of indoor atmospheres (see Section 4.5.3). The problem has also been confused by the circumstance that ozone contents of the atmosphere are high in the spring and early summer and low in the winter (see Section 4.5.2) thus apparently confirming the importance of direct sunlight.

It is also of interest to note that many workers have complained that it seems impossible to correlate indoor exposure tests, using sources of artificial light, with sunlight exposure, *i.e.*, to the atmosphere; for example, Morris, Hollister, Barrett, and Werkenthin<sup>49</sup> have examined a number of different types of carbons in attempts to produce an arc-light having the same effect on different stretched rubbers as does sunlight, and eventually admit failure. Jackson<sup>46</sup>, in summarizing his objections to the use of ultraviolet lamps, says "... the atmosphere surrounding the lamp becomes charged with ozone, which has a considerable independent action on the rubber". Kral<sup>50</sup> claims to have led ozonized air from an ultraviolet lamp to a sample stretched in darkness, and found no cracking, whereas the sample cracked readily when exposed near the lamp; he does not state how the ozonized air was led to the sample, but the ozone may well have been removed on the way unless he took special precautions, which he does not mention. He claimed that short-wave ultraviolet light was the causative factor because the sample did not crack when exposed under glass, but ozone, or ozone-forming radiation, could not then have reached the rubber.

The experiments described in Section 4.2 show that light is certainly not essential to the formation of cracks, but, on the other hand, light often plays a considerable part in preventing cracking, by forming a surface skin of oxidized rubber which prevents ozone from reaching the actual rubber surface. This effect was first understood by Williams<sup>3</sup>, who used the phenomenon to protect stretched rubber surfaces from attack by ozone; the skin-formation was hastened by the use of an oxidation catalyst, an alcoholic solution of copper chloride being painted on the rubber. This surface skin, and its protective effect, was observed by Van Rossem and Talen<sup>1</sup>, who found that exposure-cracking may be more severe on the shaded side of the sample, and Garvey and Emmett<sup>14</sup>

demonstrated the different effects clearly by showing that no surface discoloration or hardening were produced by ozonized air, whereas ultraviolet light produced both surface changes.

This skin formation is also responsible for the apparent protection provided by the use of white pigments in the rubber. Various workers have noticed that white or drab vulcanizates appear to be resistant to exposure-cracking, while the addition of quite small amounts of carbon black destroys this effect. For example, Shepard, Krall, and Morris<sup>51</sup> found that the incorporation of small proportions of carbon black reduced the resistance to cracking; Evans<sup>48</sup> showed that the addition of 1 per cent of black produced a definite increase in the amount of cracking; and Turner<sup>52</sup> demonstrated that as little as 0.5 per cent of thermatomic black produced a marked increase in cracking when added to a blanc-fixe mixing. As a result of these experiments it was argued that white rubbers reflected the light and were hence not "sun-cracked", whereas gray or black rubbers absorbed the light, the actinic energy being used in the formation of cracks. Northam<sup>53</sup>, used a somewhat different argument, contending that the white rubber reflected more light, and hence less ozone was formed at the surface.

It remained for Turner<sup>52</sup> to provide the true explanation, and he demonstrated that light had just the opposite effect: white pigments reflect much light, and hence more light is absorbed in the over-lying layer of rubber than is the case with a black vulcanizate, in which the light passes only once through the surface layer of rubber; in the case of a white rubber, light passes through the surface at least twice, or more than twice if internal reflection can occur. Thus the surface of oxidized rubber is thicker on a white rubber than on a black one, and ozone attack is relatively greater in the latter case. Turner allowed outdoor-air to reach a stretched white rubber, part of the surface of which was shielded from the light; the illuminated portions did not show any cracks, but the covered portion cracked badly, no marked difference in behavior being found when a black rubber was used.

Some workers, *e.g.*, Evans<sup>48</sup> and Turner<sup>52</sup>, have reported that magnesium carbonate provides particular protection against "sun-cracking" (not exposure-cracking), and this may be due to the greater transparency of vulcanizates loaded with this filler, owing to the similarity of refractive indices for rubber and the filler, thus enabling the formation of an even thicker skin.

The present author repeated some of these experiments with GR-S (see Section 3.4, Table I); the presence and influence of the resinous skin are described in the earlier section, and the relative efficiency of magnesium carbonate is also illustrated.

Some workers, for example, Wurm<sup>54</sup>, Ball and Bradley<sup>55</sup>, Howard and Boehmer<sup>56</sup>, and Northam<sup>53</sup>, believed that ozone was the immediate causal agency in exposure cracking, but that the ozone was produced at the surface of the rubber by the action of ultraviolet light. There seems to be no good reason to believe this contention, since the radiation most effective in producing ozone<sup>57</sup> is strongly absorbed by air, and it is stated by Meetham<sup>58</sup> that insufficient reaches the lower atmosphere to produce even the small amount of ozone found therein. Similarly, when an ultraviolet lamp is used, it would appear that the ozone is formed near the tube, and diffuses through the air to the rubber surface<sup>59</sup>.

4.6.2. *Oxygen*—Some writers believed that oxygen attack is responsible for cracking, despite the absence of cracking when stretched samples are aged

in the oxygen bomb, for example, Shepard, Krall, and Morris<sup>51</sup> say "It is thus an established fact that sun-checking or sun-cracking is an oxidation process aided by both light and heat" (see Evans<sup>48</sup>). Werkenthin, Richardson, Thornley and Morris<sup>52</sup> point out that the correlation between oxidation and sunlight aging is poor; on the other hand, the special type of oxidative increase in weight produced by acetone peroxide does seem to correlate with exposure-cracking<sup>60</sup>.

4.6.3. *Heat*—Shepard, Krall, and Morris<sup>51</sup> and Wurm<sup>54</sup> believed that heat played a part in producing exposure-cracking, but they probably mistook acceleration of the rate of cracking, on arising the temperature, for the causation of cracks by heat. Ozone would not be encountered in the Geer oven and oxygen bomb, and several workers have demonstrated that stretched rubber does not form surface cracks when subjected to these heat-aging tests<sup>61</sup>. Kearsley<sup>43</sup> showed that, at elevated temperatures, exposure-cracking was accelerated and the critical strain became lower, a change from 60° to 160° F doubling the rate; cooling reduced the rate of cracking, and freezing prevented it entirely. On the other hand, Ball, Youmans, and Rausell<sup>17</sup> found that the maximum cracking occurred at 25° C, higher or lower temperatures giving a reduced degree of cracking; these differences are no doubt related to the type of compound used, and its rate of stress decay.

Morris, Hollister, Barrett and Werkenthin<sup>49</sup> and also Northam<sup>53</sup> both draw attention to the influence of temperature on the protection produced by a wax bloom; higher temperatures may cause disappearance of the bloom, due to increased solubility in the rubber, or may increase the protection by melting the wax and causing it to flow over any cracks which may have been produced in the bloom by stretching.

4.6.4. *Humidity*—McKee and Depew<sup>47</sup> found that cracking was especially rapid on a hazy day, and suggested that this may be attributed to humidity. On the other hand, Kearsley<sup>43</sup> showed that humidity changes produced no effect on the degree of cracking, and it should be noted that in the A.S.T.M. specification<sup>44</sup> for ozone-resistance, the air is dried before it is ozonized<sup>62</sup>; this drying is probably done to ensure constancy of ozone production<sup>63</sup>, cracking can, however, certainly occur satisfactorily in dry air. The present author found that the degree of cracking was unchanged if the air was first bubbled through water, or if the air was dried, and it is thus considered that humidity does not play a part in either causing or modifying exposure-cracking. Care must be taken in interpreting the results of experiments in which the air is dried, for example commercial calcium chloride contains free alkali which removes the small amounts of ozone present in the air; the calcium chloride must first be carbonated<sup>64</sup>, after which, cracking readily occurs in the dried air.

Tuley<sup>65</sup> reports that "frosting" of unstretched rubber occurs in the presence of ozone and humidity, although he claims that small strains may actually be present in the nominally unstretched rubber.

## 5. INFLUENCE OF STRAIN ON THE FORMATION AND GROWTH OF CRACKS

Changes in the ozone concentration do not appear to produce changes in the nature of the cracking, but only influence its rate (see Section 4.5.5), and hence another factor must be responsible for the wide differences in crack distribution which may be found.

## 5.1. DESCRIPTION OF THE GROWTH OF CRACKS

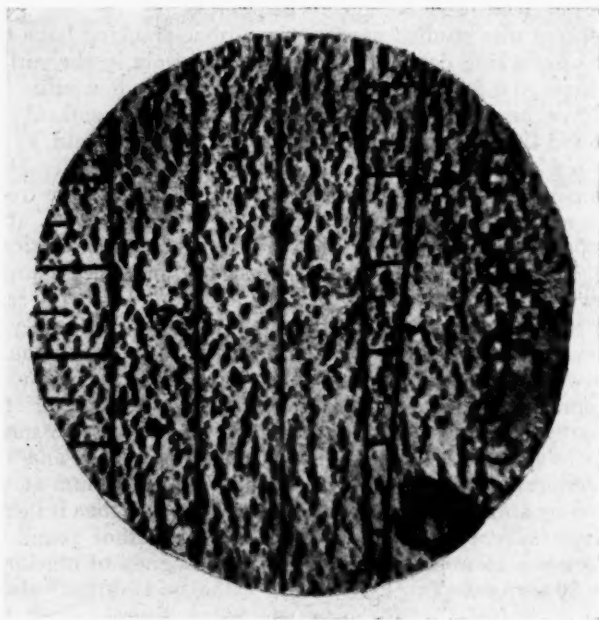
5.1.1. *Information in the literature*—Thompson<sup>66</sup> first showed that rubber must be stretched before cracking occurs, and this has since been confirmed by many other workers, for example: Haushalter<sup>16</sup>, Williams<sup>3</sup>, Chappuis<sup>67</sup>, Haushalter, Jones, and Schade<sup>15</sup>, and Van Rossem and Talen<sup>1</sup>. On the other hand, Merz<sup>68</sup> claimed that unstretched rubber cracks on exposure, but it is clear from his account that he was concerned with crazing, and not with cracking. Tuley<sup>65</sup> found that "frosting" was produced by ozone attack on nominally unstretched rubber, but this "frosting" may be of a different nature from exposure-cracking, as humidity is claimed to be an essential factor in its formation. Other effects of strain were noted by Evans<sup>48</sup>, who found that calender grain increased the degree of cracking when samples were bent along the grain, and that roughnesses in the surface caused enhancement of cracking.

Most workers who studied exposure- or ozone-cracking have realized that the severity of cracking depends greatly on the strain in the surface, appearing to pass through a marked maximum at a relatively low value of the strain, but there have been no detailed accounts of this important relationship. Williams<sup>3</sup> found the maximum cracking at 3–5 per cent strain, at which "only a relatively few cracks appeared, but these assumed considerable size". As the strain was increased, the cracks became smaller and more frequent, there being 30 per sq. cm., at 5 per cent strain, and 400 per sq. cm. at 20 per cent strain. Shepard, Krall, and Morris<sup>51</sup> found that there was a critical elongation for producing cracking, while an increase in strain "produced a large number of fine cracks which were less visible". Kearsley<sup>43</sup> found that the cracks became smaller and more frequent as the strain was increased, until they covered the whole surface. Van Rossem and Talen<sup>1</sup> found that the "maximum cracking" occurred between 10 and 20 per cent strain: above 20 per cent elongation the size of the cracks became gradually smaller, while the number still increased until, at about 90–100 per cent elongation the cracks were so small that they could hardly be seen with the naked eye. Somerville, Ball, and Cope<sup>69</sup> found that the deterioration in tensile strength showed a maximum at about 10 per cent, followed by a minimum at about 400 per cent, and then it increased again.

5.1.2. *Experimental observations*—The present author found that it was necessary to use a microscope to observe the progress of cracking at strains greater than 30 per cent (Van Rossem and Talen<sup>1</sup> and Norton<sup>10</sup> also made some microscopic observations), and he found the most rapid crack formation to occur at the highest strains, i.e., at 75 per cent or above, rather than at moderate strains. The first cracks seen (to be called protocracks) were so small that considerable magnifications were required (about  $\times 300$ ) to observe them satisfactorily, and it was also found necessary to use a transparent mixing (Mix 270). Samples shaped as in Figure 1 were exposed out-of-doors, and it was found that the protocracks (about  $1\mu$  long) could be seen after only a few hours' exposure at 75 per cent strain, while they took much longer to appear at lower strains, requiring 5 hours at 30 per cent, 9 hours at 25 per cent, and 30 hours at 20 per cent strain; thus the rate of formation of the cracks is greatest at the highest strains. Very early stages in cracking have not yet been examined in detail, and hence it is not possible to say whether, at high strains, the large number of cracks form suddenly, or are initially too small to be visible.

The growth behavior of the cracks is very complicated; collectively, growth proceeds until the cracks have opened sufficiently wide to remove the mean surface strain, but individually a crack may grow either larger or smaller,

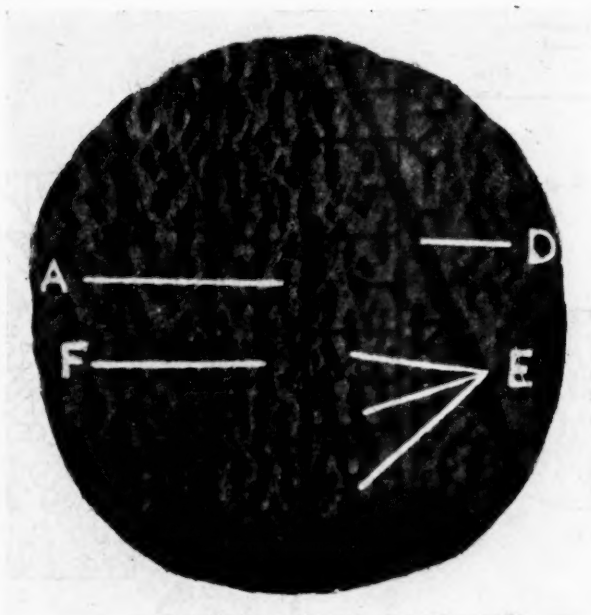
the final condition of the sample being represented by a few relatively wide cracks, while considerably more have collapsed. These phenomena are illustrated in Figures 9-12, and the relative stages in the process can be followed, on a time basis, in Figure 15, although the actual rate of cracking is different. Figure 9 comprises three photomicrographs, representing the early stages of crack growth, at a magnification of approximately  $\times 320$  ( $9a = \times 325$ ,  $9b = \times 350$ ,  $9c = \times 310$ ). As crack growth proceeded, the surface became progressively more uneven, until it became difficult to obtain a focus sufficiently good for photographic purposes; Figures 10-12 were therefore drawn with a camera lucida. Figure 10 shows the same region as Figure 9, Figures  $9a-9c$  being drawn as Figures  $10a-10c$  to make the diagrammatic series complete.



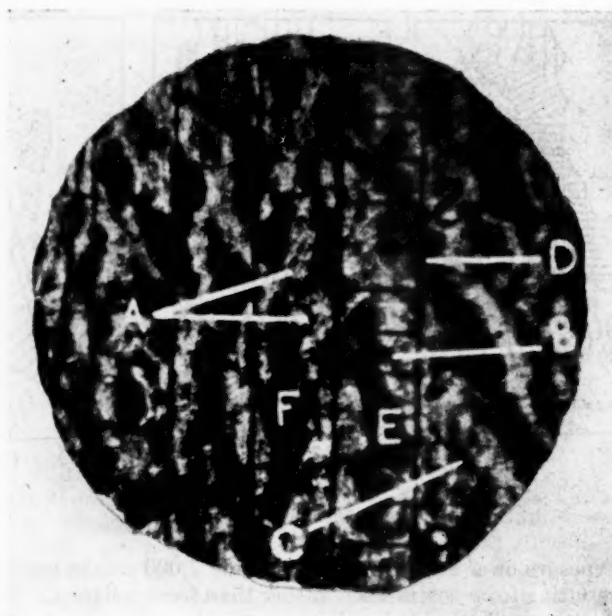
a (4 hours' exposure).  $\times 325$

In the series of drawings, some of the cracks have been cross-hatched to assist in identification. Figures  $9a$  and  $11a$  show the large numbers of protocracks which are formed at relatively high strains (say 75 per cent), there being 22,000 per square millimeter in Figure  $9a$  (4 hours' exposure), and 16,00 per sq. mm. in Figure  $11a$  after 5 hours' exposure during a normal winter day. Figure  $12a$  (20 hours' exposure) shows an early stage in the growth of cracks at 37 per cent strain, the number of cracks being only 450 per sq. mm., yet the period of exposure corresponds to four times that shown in Figure  $11a$ ; there is thus a radical difference in initial behavior at high and low strains.

The general progress of crack-growth occurring at 75 per cent strain can be seen in Figure 10, in which the magnification is  $\times 315$ ; hence, in Figures  $9a$  or  $10a$  (4 hours' exposure), none of the cracks is more than  $1/10,000$  inch wide. Figures  $9b$  and  $10b$  illustrate a later stage in development, as produced by about



b (21 hours' exposure).  $\times 350$



c (60 hours' exposure).  $\times 310$

FIG. 9.—Photomicrographs of crack-growth at 75% strain.

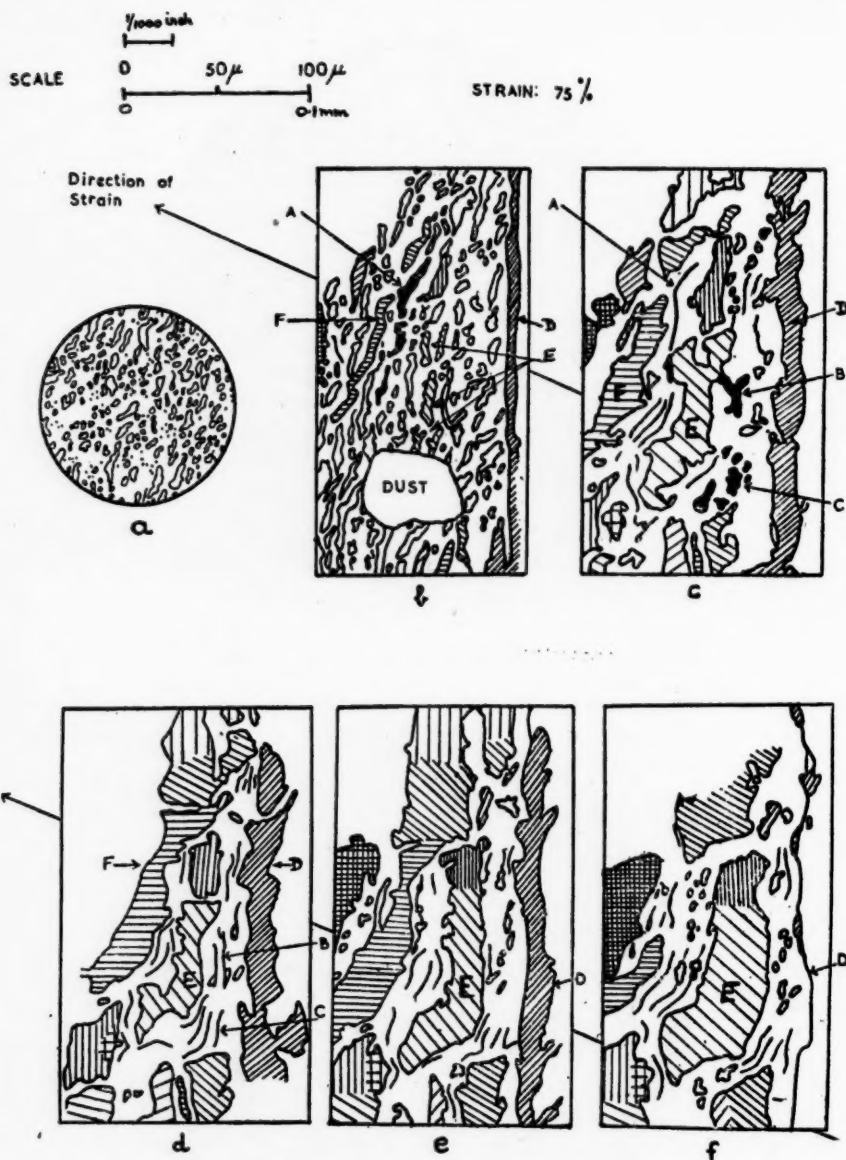


FIG. 10.—Stages of crack-growth at 75% strain. a, 4 hours' exposure; b, 21 hours; c, 60 hours; f, about 500 hours.  $\times 315$

21 hours' exposure on a winter day, there being 7,000 cracks per sq. mm., the reduction resulting from coalescence, rather than from collapse. The direction of the applied stress is shown by the arrow intersecting the drawings, and it can be seen that the cracks have now commenced to grow in a direction at right angles to the strain, with the exception of the long crack, marked "D",

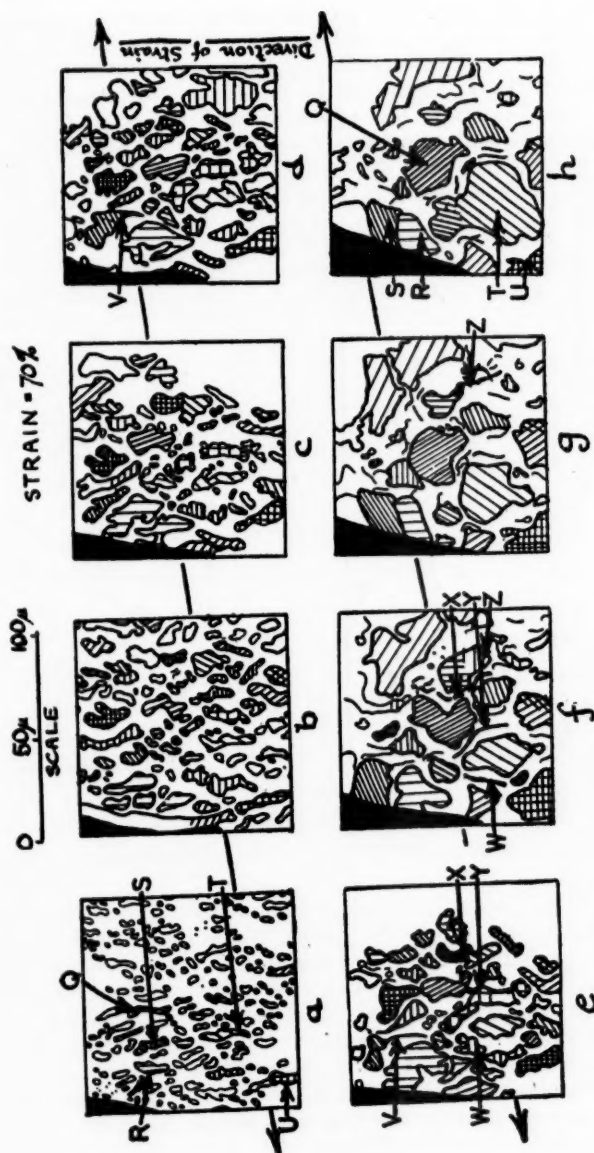
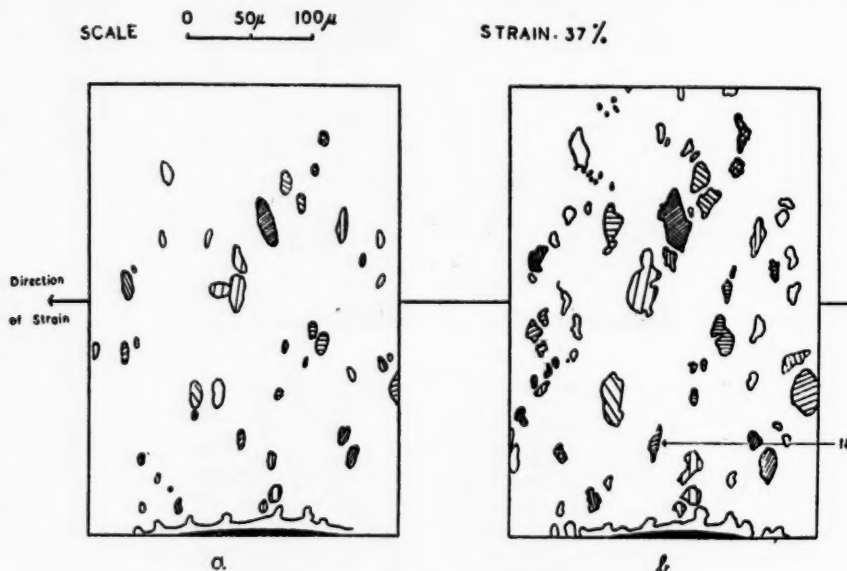


FIG. 11.—Stages of crack-growth at 70% strain. (X340)

which has formed along the ridge produced by a scratch in the mould cover-plate. Figures 9c and 10c (60 hours' exposure) illustrate a new phenomenon; there are now only 2,000 cracks per sq. mm., many cracks having collapsed in the following manner. Attention is drawn to cracks "A" in Figures 9b and 10b; in Figures 9c and 10c, crack "A" has shrunk to a mere scar because the neighboring cracks, with vertical and horizontal shading respectively in Figure 10, have expanded very considerably. At the same time, the diagonally-hatched cracks at "E" in Figure 10b have joined to form the Y-shaped crack in Figure 10c, and crack "F" has expanded, with the result that a number of cracks originally between "E" and "F" are now also represented by scars, some of which can be seen in Figure 9c. In passing from Figures 10c to 10d, cracks "D" and "F" have expanded still more, and those at "B" and "C" have col-



Early stages of crack-growth at 37% strain ( $\times 215$ ).

FIG. 12a.—20 hours' exposure.

FIG. 12b.—50 hours' exposure.

lapsed in their turn. A similar sequence can be seen in the series in Figures 10d, 10e, 10f, the long crack "D" finally succumbing as the numbers are reduced to about 200 per sq. mm. while the remainder tend to round themselves off. This "rounding" of the mature cracks is characteristic of crack growth at these high elongations, and will be discussed in Section 5.2.2. It can be seen also that, apart from the exceptional crack "D," all the final cracks can be traced among the larger cracks at quite early stages in the growth, and thus a crack which is initially larger than the remainder is at some advantage from the point of view of a continued growth; this question, also, is discussed in Section 5.2.2.

After the condition shown in Figure 10f (about 500 hours' exposure) had been reached, the tension in the specimen was relaxed, and all the remaining cracks closed up considerably, showing that stress concentrations at the bottoms of the cracks were still effective in controlling the size. The specimen was then stretched to 400–500 per cent elongation, causing cracks such as "E"

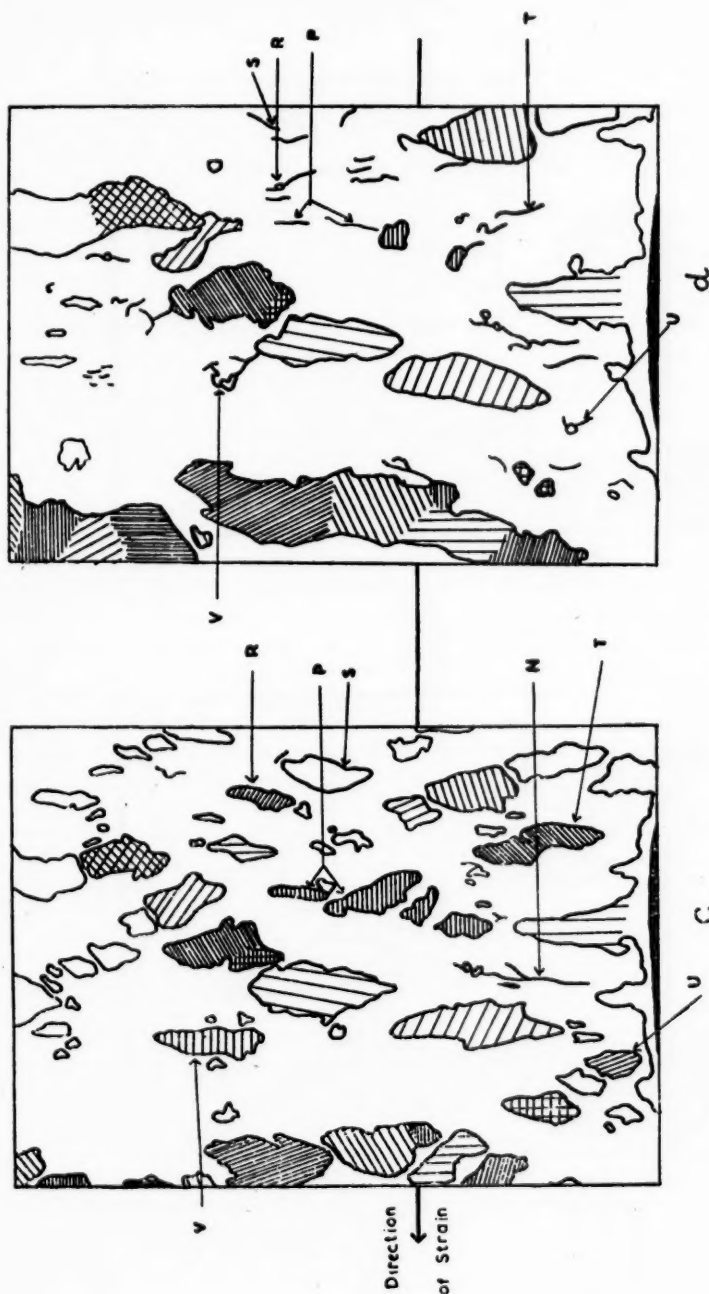
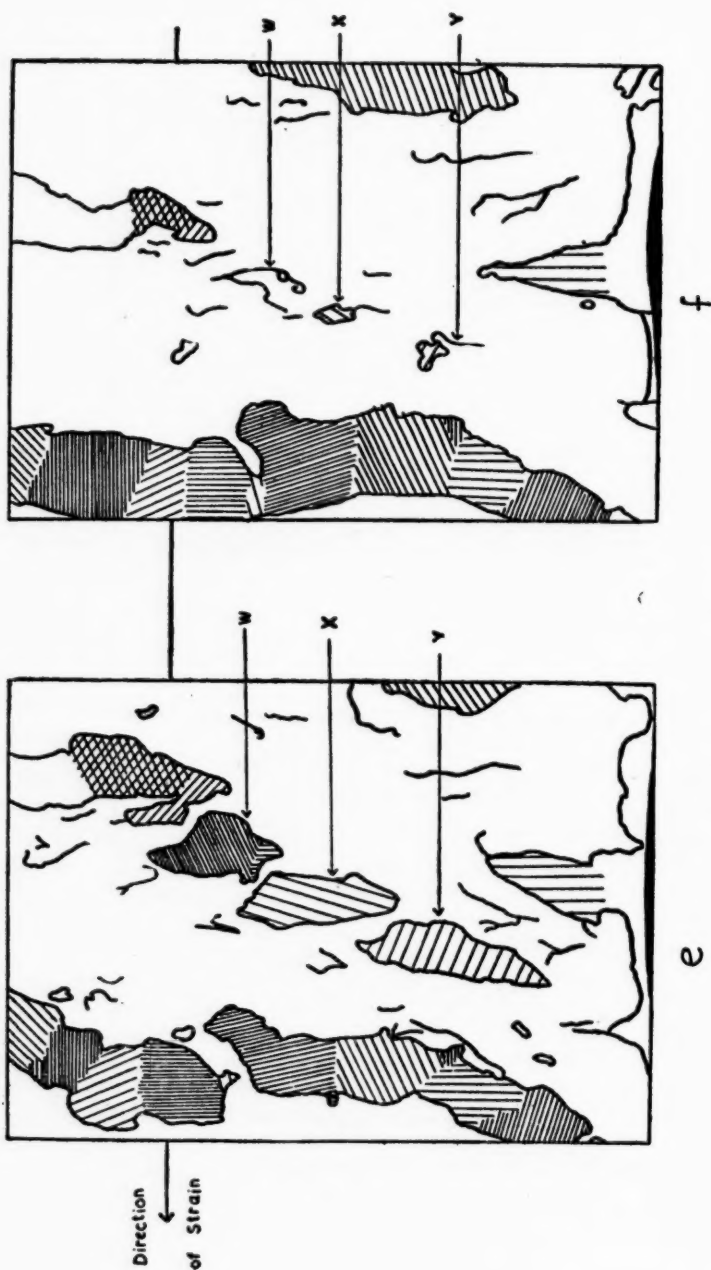


FIG. 12d.

Intermediate stages of crack-growth at 37% strain ( $\times 250$ ).  
FIG. 12c.—180 hours' exposure.



Final stages of crack-growth at 37% strain (X250).

Fig. 12f.—About 1,000 hours' exposure.

Fig. 12e.

to become considerably "wider" (parallel to the direction of stretch) than "long," yet crack "D" did not reopen. The sample was then stretched locally in several different directions by means of small forceps and dissecting needles in the immediate vicinity of crack "D", but the scar could not be reopened, and it is concluded to have "healed". At present it is possible only to speculate about the nature of this "healing" process; these transparent vulcanizates are remarkably self-adherent unless the surfaces are dusty or greasy, and it is possible that the sides of the crack are merely "stuck" together, but against this view it is considered likely that small pieces of dust would tend to collect in the cracks; in fact, the surface of the sample soon loses its tacky feel. (A large piece of dust can be seen in Figures 9b and 10b, where it lodged temporarily—its presence does not seem to have modified the cracking locally, as would be expected on the Dufraisse theory, see Section 4.4.). Alternatively, as the samples were exposed to light, and an oxidized skin had certainly formed on the less strained parts of the specimen, it is possible that crack "D" may be sealed over with oxidized rubber. Yet another possibility exists in the likelihood that the sides of the crack are covered with oxygenated chain-ends, and it is possible that oxygen-bridging of the chains could occur. On one occasion (see Figure 12f, crack "W") a crack which had collapsed during the previous night was successfully pulled open, but only by stretching vigorously; it appeared suddenly to "tear open" and, on readjustment of the strain to the original value in the sample, it assumed a shape very similar to that in Figure 12e; none of the other cracks opened, however.

Figure 11 (a-h) provides a similar series of drawings for a different sample at a high strain (magnification is  $\times 340$ ), and thus provides evidence that the behavior of the first sample was by no means abnormal. The black area on the left side of the drawings is part of an India-ink mark, used to locate the region under observation; India ink does modify the growth of cracks, but only in its immediate vicinity, by preventing cracking in the area which it covers, presumably by being impervious to ozone, and for this reason cracks tend to grow towards the ink marks (see bottom of Figure 12). Figure 11a shows the large number of protocracks and, in this case also, the larger cracks (such as the five, "Q"-"U") can be traced to the end of the series (Figure 11h). The collapse of many cracks occurs during the intermediate stages, as indicated at "V"-"Z" in Figures 11d-11g, and the cracks which remain have the rounded outline noted before; the only marked difference between Figures 10f and 11h is the rather more elongated, and hence actually longer, cracks in the former, but it is possible that the abnormal crack "D" which would have an important influence in controlling the strain distribution in the early stages, may have contributed to this effect.

Figure 12 illustrates the effect found at a much lower strain (37 per cent). Figure 12a (20 hours' exposure) shows that far fewer cracks are formed initially at this elongation (the magnification in this series of drawings is a-b,  $\times 215$ ; c-f,  $\times 250$ ). Contrary to experience at high strains, new cracks can easily be observed to arise for some time after the initial ones have been formed (compare Figures 12a, b, and c, where the numbers of cracks per sq. mm. are 450 (20 hours), 770 (50 hours), and 730 (180 hours); this effect is explained in Section 5.3.2). After the stage of Figure 12c (180 hours' exposure), marked changes occur; the larger cracks, having grown at right angles to the strain, link up end-to-end (see the large crack at the left of Figure 12d), and are thus enabled to gape open more widely, causing many cracks to collapse (see cracks "N"-"Y" in Figures 12c-12e). Although the large cracks have linked

up in this manner, complete fusion does not occur for a considerable time, as very thin septa can be detected at the boundaries of the hatched areas in Figures 12c and 12f; these septa gradually decrease in height, and recede to the bottom of the crack. Another respect in which cracks at this strain differ from those at higher strains, is that those cracks which survive the eliminating process do not tend to become rounded in outline, but continue to grow and link up (see crack at left edge of Figure 12f; about 1,000 hours' exposure) to form cracks eventually several millimeters long. A discussion of this crack growth at lower strains is given in Section 5.3.2.

## 5.2. DISCUSSION OF THE OBSERVED PHENOMENA

5.2.1. *Influence of strain on the number of cracks formed*—The number of cracks per sq. mm. at different strains and after different periods of exposure out-of-doors during the winter, are given in Table II and are plotted in Figure 13. It can be seen from Figure 13 that, during the early periods of exposure,

TABLE II  
RELATION BETWEEN NUMBER OF CRACKS PER SQ. MM. AND SURFACE STRAIN, AFTER DIFFERENT PERIODS OF EXPOSURE

Surface strain (%)	Number of cracks per sq. mm. after exposure for (hours).						
	21	51	81	24	56	300	600
15	—	—	—	—	—	—	15
21	—	—	—	15	48	25	18
23	—	—	4	10	180	36	27
25	—	—	11	52	300	51	31
26	—	—	22	170	360	47	43
29	—	—	26	410	360	72	52
32	—	7	120	450	300	72	51
35	—	300	?	600	480	134	82
40	—	2,200	3,000	970	600	191	125
43	7,500	5,200	3,000	1,500	?	360	210
45	6,700	5,600	2,600	1,100	600	300	220
51	13,400	6,700	3,000	1,900	900	330	240
56	20,000	8,200	4,100	1,900	?	?	260
60	24,000	8,200	4,500	1,900	1,270	630	250
67	26,000	10,100	4,900	1,900	1,340	900	420
71	30,000	11,200	5,200	2,240	1,280	720	360

A dash (—) in the table indicates that very few cracks were present.

the number of cracks increases by a factor of at least ten-fold when the strain is increased from 30 to 50 per cent, and very large numbers of proto-cracks, of the order of 30,000 per sq. mm., are formed after a few hours exposure at strains greater than 75 per cent. It is difficult to carry out observations at strains greater than about 100 per cent because the minute cracks, and the crystallization produced in the rubber by stretching, combine to scatter much light and render observation difficult. Although Table II extends only to 70 per cent strain, less complete data are available from other samples for higher strains, and some of these results have been added to Figure 13.

Figure 14 illustrates the marked difference in behavior found between strains greater than, and less than, (say) 50 per cent, and shows how (1) at strains lower than 50 per cent, the number of cracks passes through a maximum and then decreases as the smaller cracks either coalesce or disappear; (2) the maximum occurs earlier, the higher the strain; and (3) the rate of crack

formation is much less at the lower strains, especially at strains below 40 per cent.

5.2.2. *Influence of strain on the size of the cracks*—It is important to distinguish between the rate of formation and the rate of growth of cracks. It can be seen from Figure 13 that the rate of formation of cracks is very low at strains lower than 30 per cent, and increases rapidly as the strain is increased until, at about 70 per cent strain, the rate of formation of cracks becomes inde-

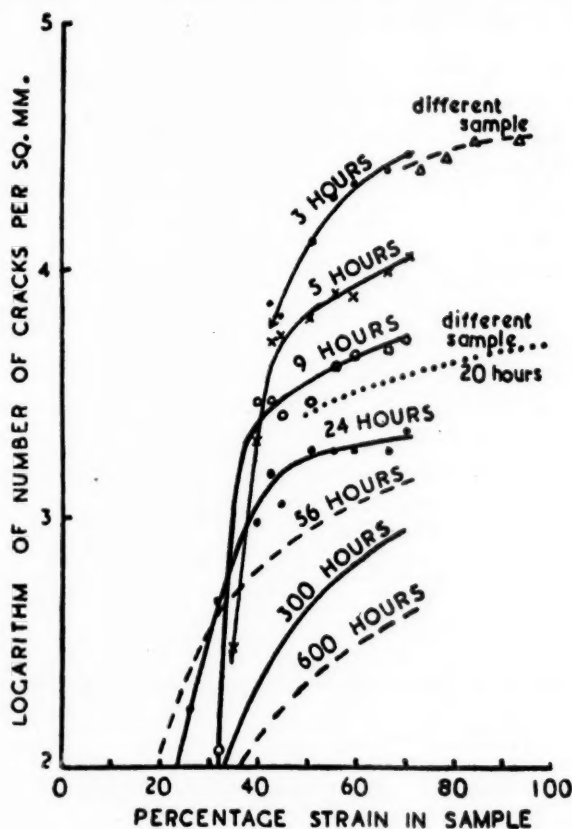


FIG. 13.—Relation between number of cracks per sq. mm. and original surface strain, after different periods of exposure.

pendent of strain. The rate of formation of the proto-cracks thus depends on the strain in the surface, and if the strain is low (say 30 per cent), they will be formed infrequently. Once the proto-crack is formed, however, it is pulled open in the direction of the strain, with the result that there are stress concentrations at the ends of the crack, the stress there being higher than in the surrounding area of uncracked rubber. Crack formation will now occur more rapidly in these stress concentrations, the new proto-cracks being quickly absorbed into the existing one, and thus constituting crack growth. It is thus clear that, at strains less than about 75 per cent, the initial rate of crack growth

will be greater than the rate of crack formation, the difference in rate being greater the lower the initial surface strain.

A corollary of this stress concentration at the end of the crack is that the growth always takes place at right angles to the direction of applied stress. Many authors have drawn attention to this characteristic of cracking. Norton<sup>10</sup> used the phenomenon to study the stress distribution in the ends of the normal dumb-bell shaped tensile test-specimen; he also showed that a reticulate type of cracking was produced when the stress was uniform in all directions, as is the case with a sheet of rubber stretched over a ball.

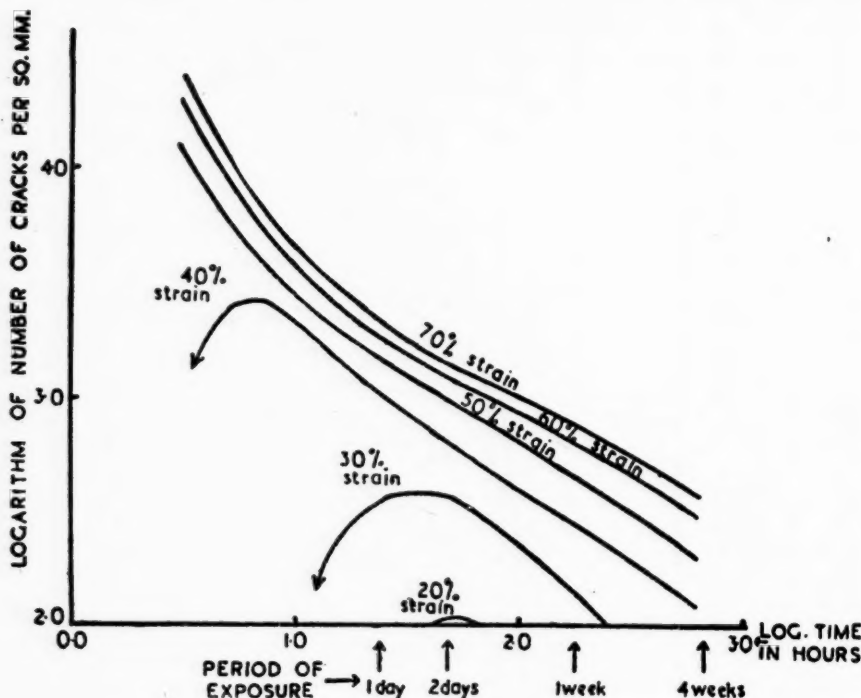


FIG. 14.—Relation between number of cracks per sq. mm. and period of exposure, for different initial surface strains.

The manner in which changes in strain control the initial rate of crack growth have been discussed above, but very important effects occur later which limit the subsequent rate of growth, and produce the phenomena associated with the "critical elongation"; these factors will be discussed in a separate Section (5.3), but two other effects must be considered here, *i.e.*, the factors controlling (1) the collapse of cracks, and (2) the "rounding" of cracks at high strains.

(1) It was shown in Section 5.1.2 that cracks which are initially larger than the majority appear to be at some advantage from the point of view of continued crack growth, while the smaller ones collapse; this results from a combination of two effects. Suppose that there are two cracks which have recently grown large, lying opposite one another and at right angles to the applied stress,

and that there are a number of smaller ones between them. In the first place, that part of the applied stress which is intersected by the two large cracks will be concentrated at, and supported by, their ends, and can thus no longer cause the small cracks to grow any larger. Secondly, the large cracks will now grow more rapidly than before, and hence will open more widely, thus relieving the stress which has been holding the small cracks open, and the latter will conse-

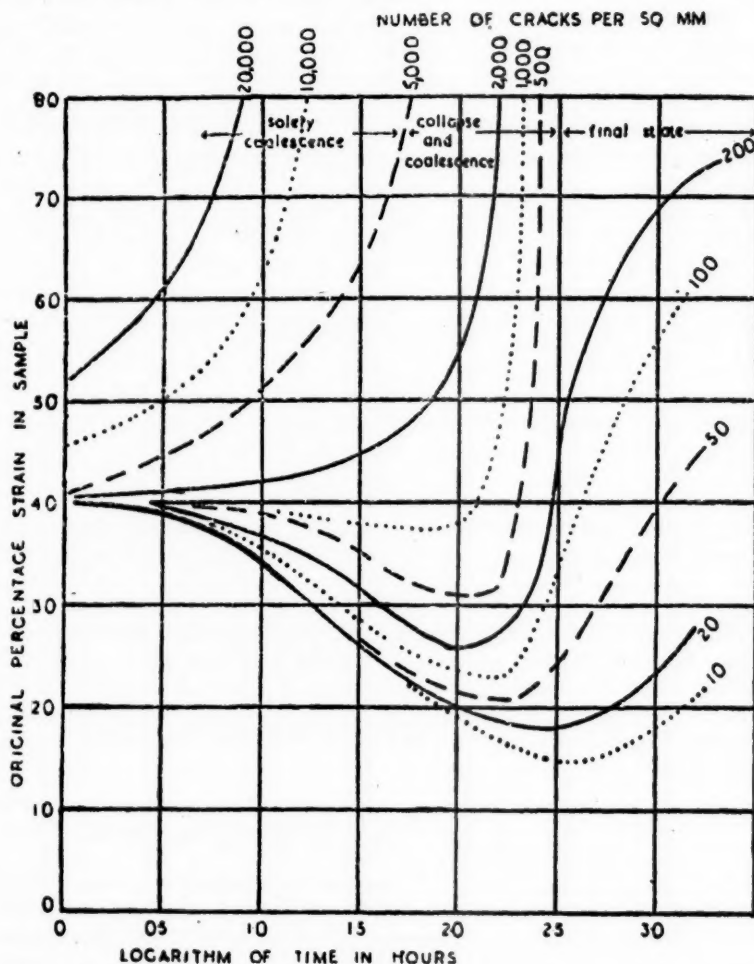


FIG. 15.—Relation between number of cracks per sq. mm., surface strain, and log. period of exposure.

quently close. This phenomenon can easily be demonstrated by stretching a thin strip of rubber, and making a small cut through it at right angles to the direction of stretch; if much larger cuts are now made each side of the small cut, *i.e.*, nearer to the ends of the strip, the latter will at once close. The larger the crack is initially, the less likely it is to be shielded by other cracks and hence, as is described in Section 5.1.2, it is possible at an early stage to recognize those

which survive. It should be noted also that if a large number of cracks are very close together, part of a large crack may lie in a region rendered devoid of stress, and will thus collapse, as occurred with crack "D" in Figure 10.

(2) As the cracks gape open the surface strain is reduced, and crack growth ceases when the strain reaches a low value. It might be expected that low strains would be removed in this way more quickly than would high strains, but it is observed that crack growth ceases earlier at high strains than at low ones. This is illustrated in Figure 15, in which the abscissa is the logarithm of the period of exposure in hours, and the ordinate is the original strain in the sample, the lines on the graph representing equal numbers of cracks per sq. mm. Suppose the sample has an original strain of 75 per cent; a large number of protocracks (more than 30,000 per sq. mm.) are formed in a few hours, but these soon coalesce so that the number is reduced to 20,000 after about 9 hours (the data in Figure 15 were obtained with a different sample from that used for Figure 13, the rate of cracking being considerably greater in the latter case). Coalescence of the cracks continues until the number has decreased to about 5,000 per sq. mm., *i.e.*, approximately equivalent to the stage shown in Figure 9b. After about 50 hours' exposure, marked collapse of cracks occurs, as well as coalescence, and the number of cracks decreases to somewhat less than 500 per sq. mm. after about 300 hours' exposure. After this stage is reached, conditions become stabilized, and further crack coalescence or collapse is infrequent, the final number of cracks being a little less than 200 per sq. mm., as is shown in Figures 10f and 15. On the other hand, at (say) 20 per cent strain the first cracks do not appear until about 50 hours' exposure has elapsed, and the maximum number of cracks is found after about 300 hours' exposure, *i.e.*, when conditions have become nearly stable at 75 per cent strain. After this period, when the surface strain is practically absent at high elongations of the sample, but not at low elongations, the difference in strain is supported by the body of the sample. At the high strains, therefore, the cracks exist in a strain-free surface, but are held open by stresses in the thickness of the rubber. If a cut in a sheet of rubber is subjected to a high stress, it becomes rounded, and hence the cracks, when no longer controlled by strains in the surface, will be likely to become rounded where high strains are present in the body of the sample; this "rounding" of the cracks at high strains was described in Sections 5.1.2, and will be shown to have an important effect on the growth of cracks at different elongations of the sample.

### 5.3. EXPLANATIONS OF THE "CRITICAL ELONGATION" AT WHICH DETERIORATION IS MOST SEVERE

5.3.1. *Theories in the literature*—Dawson<sup>70</sup> suggested that the optimum tension at which cracking is most severe (see Section 3.1), might be explained by reduction in permeability, and hence oxygen accessibility, caused by stretching the rubber; at that time it was thought that oxygen played a part in causing cracking, but the active agency is now known to be ozone (even if it only catalyzes oxygen attack) and it is inconceivable that a gas which attacks rubber so vigorously could diffuse in the material for any distance. Cotton<sup>71</sup> remarked that the rubber molecule was a spiral, and the greatest amount of work was required to start the opening of the spiral; he imagined the possibility that the rubber molecule was in its most unstable condition when the rubber was stretched about 10 per cent. On the modern view of the rubber molecule as a randomly kinked chain, taking up its configuration at any particular moment

as a result of thermal motion, it is difficult to believe that the small deformations required for the critical elongation could produce a change in the intramolecular configuration sufficient to alter its chemical reactivity to such an extent. In this connection, Williams and Dale<sup>72</sup> concluded that stretching does not alter the vibrational characteristics of the C—C bond until 400 per cent elongation is reached, and that even greater elongations are required to modify the C=C frequencies.

Chappuis<sup>73</sup> noted that stretched rubber did not crack in ozonized oxygen if it had first been wetted with benzene (this is contrary to the findings of Fisher, quoted by Tuley<sup>65</sup>), and he concluded that cracking did not occur because benzene "prevented the assumption of a crystalline structure which normally occurs with tension". Van Rossem and Talen<sup>1</sup> also suggested that the critical strain might be related to crystallization on stretching, but they realized that the strain required to produce crystallization, detectable by x-ray diffraction, was many times that encountered at the critical elongation. Haushalter, Jones, and Schade<sup>15</sup> plotted the hardness of stretched rubber against strain, and found a sudden increase of hardness at small strains; they conclude that there is "some progressive change in the structure of the rubber which renders it at a certain point unusually susceptible"; the same remarks about the unlikelihood of suitable changes in molecular structure apply in this case also. Potter<sup>22</sup> stated that "ozone attacks rubber violently at low elongations, but it has a more nearly negligible effect at higher elongations"; actually, the reverse is true, crack production being more rapid at high strains.

5.3.2. *New theory advanced to account for the "critical elongation"*—It can be seen from Figure 15 that at high strains (say 75 per cent), the number of cracks is initially very high, and does not decrease to much less than 200 per sq. mm. On the other hand, at 20 per cent strain, the number of cracks is never as great as 50 per sq. mm. There is thus a profound difference in density of the populations of cracks at these two elongations, and it is believed that therein lies the explanation of the "critical elongation". Except at the very lowest strains and after long periods of exposure (where a special case exists as the mature cracks remain pointed), the cracks are, roughly speaking, four times as long as wide. Suppose, for simplicity, that the cracks are rectangles, four times as long as wide, and that there are  $n$  such rectangles, of average width  $w$  per sq. mm. of the stretched surface (the cracks can be counted satisfactorily only in the stretched state). The cracks lie with their long side at right angles to the direction of strain, and hence any line, drawn parallel to the direction of strain through a region of unit width, will have a probability of  $4w$  of intersecting any given crack (because the length of a crack is  $4w$ ). If the line is of unit length, it will cross a unit square (which contains  $n$  cracks when the unit is a millimeter), and hence it will intersect  $4wn$  cracks in 1 mm. square of stretched surface.

If the strain in the surface is  $s$ , the maximum extent to which the stretched square could relax, in the direction of the strain, is  $\frac{s}{1+s}$  mm. The  $4wn$  cracks, intersected by the line described above, produce relaxation of strain as they gape open, the maximum width ( $W$ ) being attained when the strain is completely relaxed, i.e.,  $4nW^2 = \frac{s}{1+s}$ , whence the final width ( $W$ ) =  $\frac{1}{2} \cdot \frac{\sqrt{s}}{\sqrt{1+s\sqrt{n}}}$ , and the final length ( $L$ ) =  $\frac{2\sqrt{s}}{\sqrt{1+s\sqrt{n}}}$ , the values being multiplied by 1,000 to

obtain the dimensions in  $\mu$ . This conclusion can be examined for the regions shown in Figures 9c, 10f, and 12c, but only approximately, as the cracks in Figures 9c and 12c are not in their final state, the former being chosen because it is an actual photograph of cracks, and the latter because it is the last drawing, for a region of low strain, in which a reasonable number of complete cracks are present. As is shown in Table III, the approximate expressions for  $W$  and  $L$  are in fair agreement with the actual dimensions of the cracks, bearing in mind that the cracks are neither rectangular nor identical in size.

If it is accepted, as a rough approximation, that the length and width of the cracks are functions of  $\frac{\sqrt{s}}{\sqrt{1+s\sqrt{n}}}$ , it will be of interest to determine how the value of this function changes with initial strain in the surface using, for example, the data given in Table II for 600 hours' exposure. In Figure 16 the values have been plotted against the initial strain, and it can be seen that the quantity is constant at high strains and increases rapidly at elongations below about 40 per cent to pass through a maximum at about 20 per cent strain; thus, for the sample used, the cracks should reach their maximum size of 20 per cent strain, *i.e.*, at exactly the "critical elongation"; the curve is, in fact, similar to that shown in Figure 6a for 24 days' exposure. Thus, it is believed,

TABLE III

Fig.	$n$	$\sqrt{n}$	Length ( $\mu$ )		Width ( $\mu$ )	
			$L$	actual value	$W$	actual value
9c	2,000	45	30	40-110	7	10-20
10f	176	13	100	150	25	30
12c	730	27	40	30-90	10	12-30

(N.B.—These cracks are not in their final state.)

the greater growth tendency at the "critical elongation" is a result of the geometry of the distribution of the cracks, the small number produced at this elongation being unable to relieve the strain without gaping open more widely than do those at higher strains.

The argument based on Figure 16 predicts a three-fold increase in length of the crack in passing from 70 per cent elongation to 20 per cent, but the actual increase is ten-fold or greater. There is, however, yet another factor which contributes to the increased length of cracks at low strains. Cracks at low strains must grow larger than those at high strains, and thus surface strains persist much longer at low elongations than at high ones; this relative persistence of strains at low elongations is responsible both for the continued appearance of new cracks at these elongations and for their longer growth period compared with those at high strains, both of these effects having been observed in Section 5.1.2. The persistence of stress concentrations at the ends of cracks at low strains, long after they have ceased at high strains, permits crack coalescence to occur at these elongations (as was observed in Figure 12f), but not at the higher elongations (see Figures 10 and 11); *i.e.*, cracks with pointed ends can coalesce more readily than those with rounded ends, and can thus attain very much greater length as several long cracks join together.

This argument is an oversimplification, as no account is taken of the depths of the cracks. Stress concentrations are present at the bottoms of the cracks, and the latter will therefore continue to grow downwards, but the ozone must

now diffuse down the narrow cracks, the walls of which, although not under much strain, absorb ozone (see Section 6.1) and may also collect dust; the narrower cracks at high strains are thus more efficient in preventing ozone from reaching the bottom of the crack, and they remain shallower. After 5 minutes' exposure to the ozonized oxygen, referred to above, the cracks at 75 per cent strain were about  $200\mu$  deep, whereas those at 20 per cent strain were  $750\mu$  deep.

5.3.3. *Evidence supporting the theory*—The relatively greater rate of growth of cracks at high strains, and the limitation of the final size by the effect of crowding, are important features of the theory advanced to explain the "critical elongation", and it will be useful to consider other consequences of this new view. It was shown in Section 3.4 (see Table I) that white rubbers appear to provide protection against cracking during short periods of exposure, but subsequently fail surprisingly rapidly at relatively high strains (approximately 100 per cent); a similar phenomenon is found when carnauba wax is used in the mixing (see Figure 7b). The following explanation is advanced to account for

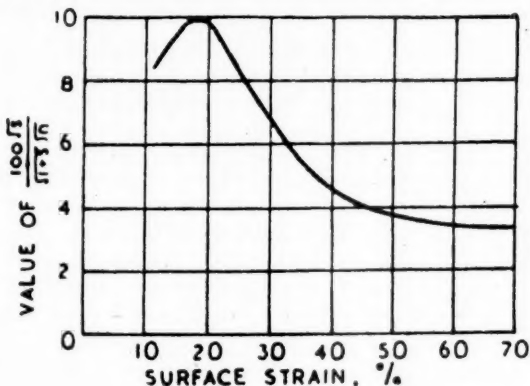


Fig. 16.—Relation between  $\frac{100\sqrt{s}}{\sqrt{1+s\sqrt{n}}}$  and strain.

both of these phenomena: in both cases the protection at low strains is produced by a surface film which is impermeable to ozone; the white vulcanizates have a skin of oxidized rubber (see Sections 3.4 and 4.6.1), while carnauba wax produces a surface bloom. When the vulcanizates are exposed in the stretched state, the relatively inelastic carnauba wax film breaks at high strains, while the oxidized films on the white rubbers crack after some four weeks' exposure; in each case ozone is then able to reach the rubber surface at a few points in the region subjected to high strain and the resulting cracks, being unhampered in growth by the presence of the many thousand neighboring cracks which would have been reducing the surface strain, grow at the rapid rate characteristic of this region of high strain, with the result that the specimen is cracked right through in a few days. Carnauba wax thus appears to increase the susceptibility of the rubber to attack by ozone. Garvey and Emmett<sup>14</sup> found that some oils "impaired the sunlight-resistant properties of the rubber, and increased the degree of cracking", and they pointed out that failure of the protective film will produce a deeper crack than otherwise "due to a concentration of stress . . . where a slight crack has developed. This stress concentration does not occur in unprotected compounds because of the larger number of

cracks formed initially. Consequently these cracks are not so deep as the isolated ones formed in compounds containing waxes".

From Table II it can be seen that, for very short periods of exposure, no cracks are found at low strains, and it could be concluded from this evidence that the critical strain occurred at the highest elongations; the cracks are, however, too small to be visible by the unaided eye. In the case of mixings containing five parts of paraffin wax, the bloom doubtless acts as a physical barrier to the diffusion of the ozone to the rubber surface, and the amount of ozone which penetrates is small, as the rubber has to compete for ozone with dust on the surface, and possibly also with unsaturated materials in the thickness of the film. If the quantity of ozone reaching the surface is small, fewer cracks are formed during a given period of exposure, but the relative numbers at different strains remains unaltered, *i.e.*, the rate of formation is merely retarded. When 5 parts of paraffin wax are added to the mixing, as in Mix 174, a coherent bloom is formed on the surface; when the rubber is stretched, the bloom becomes thinner at high strains than at low strains, and the retardation of the rate of cracking is therefore least at high strains. Thus, after considerable exposure and as a result of the general retardation, the sample would be in a condition similar to the unprotected mixing after short exposure, *i.e.*, with an apparent critical elongation at the highest strains, with the exception that the smaller retardation occurring in this region permits the cracks to be relatively bigger, and now readily visible, so that they can be graded; compare Mixings 170 and 174, in Figure 7a, which show that the retardation of cracking by 5 per cent wax is less at high strains than at low ones.

If the amount of paraffin wax is reduced to two parts, the film may be so thin that it tears at the highest strains, allowing growth of pointed cracks in this region; the sample thus behaves like the one containing carnauba wax (compare Mix 173, Figure 7a with Mix 181, Figure 7b); the rate of cracking at high strains now appears to be accelerated rather than retarded (compare Mixings 170 and 173, Figure 7a), while at strains of less than 40 per cent, retardation occurs as a result of greater thickness of the uncracked bloom. Mixings containing 1 part of paraffin wax probably form a "patchy" bloom on stretching, the uncovered parts cracking in the normal way, while the small degree of protection produced in the covered parts has the effect of increasing the value of the critical strain. It should be noted that in the case of the really successful protective waxes, which repair damage to the bloom, an apparent critical elongation of more than 100 per cent can easily occur, despite the uniform rate of formation at strains greater than 75 per cent, because high stress concentrations are more persistent at the ends of cracks at (say) 150 per cent strain than at (say) 75 per cent strain.

No study has yet been made of the relation between strain and the number of cracks formed in the case of Neoprene, and such will be necessary before its behavior is understood completely. This synthetic rubber takes up ozone much less rapidly than does natural rubber, due to protection of the double bond by the chlorine atom (see Section 6.3), and cracks thus form much less readily; the behavior may therefore be somewhat similar to that found in the case of 5 parts of paraffin wax, *i.e.*, the critical elongation is at the highest elongations. This cannot, however, be the entire explanation, as severe cracking can be produced in Neoprene by the use of ozonized oxygen (see Figure 6h), yet there is still no typical "critical elongation". Further work will be carried out on "pure-gum" Neoprene vulcanizates, to determine the actual course of crack growth.

#### 5.4. COMPARISON BETWEEN THE RESULTS OF VISUAL GRADING AND MICROSCOPIC OBSERVATION

The relation between the graded value of the cracking (see Section 2.3.1), and the number of cracks per sq. mm., is very complicated, depending on the strain in the sample and the period of exposure. Figure 17 provides the data for a discussion: this figure is drawn in the same way as is Figure 14, the abscissa being the logarithm of the period of exposure, and the ordinate the logarithm of the number of cracks per sq. mm.; the thick lines converging towards the right represent conditions of equal strain, while the hatched areas bounded

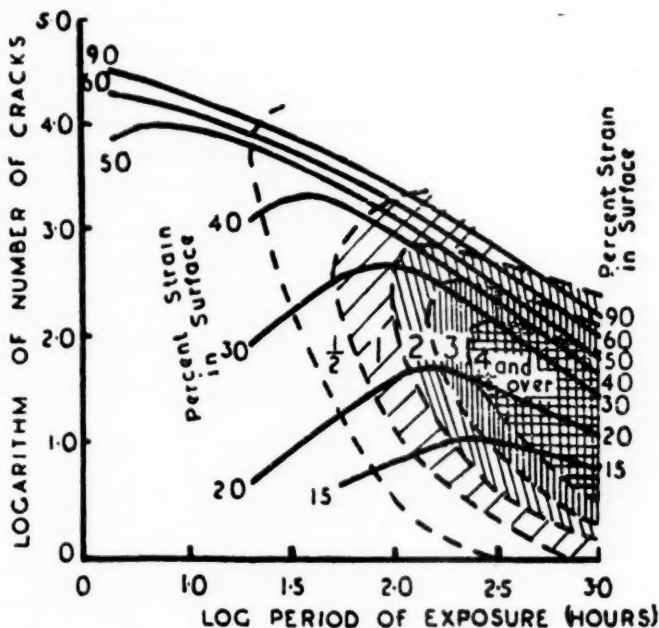


FIG. 17.—Relation between visual grading of the sample and number of cracks, surface strain, and period of exposure.

by broken lines represent conditions of equal grade value, heavier shading representing more severe cracking. It can be seen that:

(1) After any period of exposure, equal gradings can be obtained at either high or low strains, the region of heaviest shading following the line for 25 per cent strain; this effect can also be seen from Figures 6a-6f by drawing lines parallel to the abscissa.

(2) At any strain, the grade value increases as the period of exposure is increased, the thick lines converging into the more heavily shaded areas.

(3) Lines of equal grading diverge to the right, indicating that, as deterioration proceeds, a given number of cracks usually represents a more severe degree of cracking. This is the result of the increase in width of the cracks. Thus, at both low and high strains, fewer cracks are required to produce the same grade of cracking at a later exposure, but at high strains the number of cracks at any grading may increase slightly before decreasing.

## 6. PHYSICO-CHEMICAL PHENOMENA INVOLVED IN THE CRACKING OF RUBBER BY OZONE

## 6.1. INFLUENCE OF OZONE ON UNSTRETCHED RUBBER

6.1.1. *Information in the literature*—There seems to have been a tendency for some workers to make an implicit assumption that ozone does not attack unstretched rubber; examples of this will be given in Section 6.4.3, but there is actually very little direct evidence on this point in the literature. H. L. Fisher is quoted by Tuley<sup>65</sup> as finding "that a sample of unstressed pure-gum stock in ozonized oxygen gained 0.2% of its weight in 6 hours at room temperature"; he also noted that after this exposure it was bent, but showed no cracks, even under microscopic examination. Kohman<sup>74</sup> exposed a sample of unstretched rubber to ozonized oxygen of unstated concentration; he found that the rate of uptake of ozonized oxygen was distinctly different from that of pure oxygen, the rate of absorption of the former being at first much more rapid and then (after 500 hours' exposure) much less rapid, than for pure oxygen. In addition, the maximum uptake was considerably less than with pure oxygen, and the reaction was concluded not to be autocatalytic, as was considered to be the case with oxygen. During the later stages of absorption "The ozonized oxygen was replaced by pure oxygen to determine whether pure oxygen would be taken up at the normal rate, but no change in absorption was noted. The results indicate that ozone causes a permanent change in the rubber, protecting it against the action of oxygen". He also suggests that the action of ozone on rubber prevents the formation or accumulation of the catalyst responsible for the autocatalytic nature of the oxygen reaction, and he goes even further to suggest that it might be possible to improve the aging of rubber by giving it a preliminary treatment with ozone.

Van Rossem and Hessels<sup>27</sup> found that ozone, even in concentrations of 0.01 per cent or less, causes a strong Russell effect in both raw and vulcanized rubber in the unstretched state. Apart from this meagre information, the only other evidence in the literature is that ozone readily attacks rubber in solution, although this is rather a special form of unstretched rubber.

A number of investigators have reported that ozone does not produce cracks in unstretched rubber (see Section 5.1.1), while Haushalter<sup>16</sup> and Haushalter, Jones and Schade<sup>15</sup> found that the tensile strength was not decreased after exposure, even for 18 hours, in a concentration of 2-5 per cent ozone.

6.1.2. *Experiments on ozone absorption by unstretched rubber*—The information in the literature suggests that some ozone is absorbed by unstretched rubber, but it is important to have actual quantitative data on this point, and several experiments have been carried out to this end. Samples were exposed to ozonized oxygen with a concentration of  $1.0 \times 10^{-3}$  cc. per cc., the mixture of gases being passed over the sample, and the ozone uptake being determined by difference between the concentrations before and after the rubber was inserted in the gas stream. For the first experiment, a piece of commercial rubber tubing was used, and it was found to absorb no ozone in the unstretched condition and the sample did not crack, whereas the absorption was rapid and the cracking extensive when the tubing was stretched over a glass rod. It was suspected that the failure to absorb ozone might be due to an impervious bloom, and new samples were exposed after wiping with petroleum ether, and drying at room temperature overnight. In this case, a small amount of ozone was absorbed at first, but the uptake decreased continually during the first 20 minutes, and the sample did not crack. The total uptake of ozone was  $4 \times 10^{-5}$

gm. per sq. cm., *i.e.*, equivalent to a layer of the gas 0.02 cm. thick, or to saturation of all the double bonds to a depth of  $0.5\mu$ .

The amount of ozone absorbed was so very small that other estimations were used as a check on the amount. Samples of Mix 270 were cleaned with petroleum ether and exposed to the ozonized oxygen in the unstretched state, giving an absorption of  $3 \times 10^{-5}$  gm. per sq. cm. The uptake of another sample was determined by direct weighing on a microbalance, but it was found that precleaning with petroleum ether had to be abandoned, owing to the slow changes in weight which occurred over a long time as the sample dried out; 4 g. of Mix 270, with an area of 35 sq. cm., increased in weight by 0.92 mg., after exposure to the ozonized oxygen for 15 minutes. This increase cannot be compared with that found by Fisher (see Section 6.1.1), because the area of his sample is not known, and the increase on a weight basis is misleading; the superficial absorption was  $2.6 \times 10^{-5}$  g. per sq. cm., equivalent to a film of pure ozone 0.012 cm. thick. At the same time, another sample was exposed to pure oxygen, and no uptake could be detected. It thus appears that a surface film of ozonide is formed which limits further attack by ozone, and it seems likely that all the ethylenic linkages to a depth of  $0.5\mu$ , are destroyed during this process. It should be noted that there is evidence that ozone will also attack saturated linkages<sup>75</sup>.

## 6.2. INFLUENCE OF OZONE ON STRETCHED RUBBER

6.2.1. *Information in the literature*—The extensive information on the production of cracks in stretched vulcanizates is reviewed in Section 5, this section being restricted to information of a more chemical nature.

Haushalter, Jones, and Schade<sup>15</sup> found that ozone produced cracks in stretched raw smoked sheet, while Fisher<sup>65</sup> found that bent strips of ebonite, 0.5 mm. thick, with a vulcanization coefficient of 43, cracked in less than two minutes in ozonized oxygen; the latter observation may be important in view of the prevalent belief that ozone attacks only points of unsaturation in the rubber molecule (see also Section 6.1.2). Van Rossem and Talen<sup>1</sup> exposed samples of stretched rubber to ozonized air, using a concentration of  $3 \times 10^{-5}$  cc. per cc., and found that 90 per cent of the ozone was removed by the sample. Ball, Youmans, and Rausell<sup>17</sup> exposed an assemblage of rubber samples, stretched to different elongations, to ozonized air at different temperatures. The concentration of ozone was reduced from  $1.4 \times 10^{-4}$  cc. per cc., to  $1.5 \times 10^{-5}$  cc. per cc., at  $70^{\circ}\text{C}$ , or to  $8.4 \times 10^{-5}$  cc. per cc., at  $-50^{\circ}\text{C}$ , but their data do not enable the ozone uptake to be calculated. Norton<sup>10</sup>, using an ozone concentration of  $2 \times 10^{-2}$  cc. per cc., wrapped rubber tape "around a thermometer bulb, the wrapping giving tensile stress. The temperature rose from  $32^{\circ}$ – $39^{\circ}\text{C}$  in 30 seconds, when the rubber, disintegrating, fell away from the bulb".

The stresses in the rubber need not be produced by stretching to cause visible signs of deterioration; Baggish and Meade<sup>45</sup> found "crumbling" on surfaces under compression, which continued until the pressure was relieved, and Norton<sup>10</sup> found that a "feathery disintegration product" was produced on surfaces under compression.

6.2.2. *Experiments on ozone absorption by stretched rubber*—These experiments were found to be of a difficult nature and liable to error from the various sources discussed below: ring- or tube-shaped samples were not available and hence strips  $4.5 \times 1.5 \times 0.25$  (cm.) were held stretched by pegs inserted

through holes near the ends, and there was thus always some unstretched rubber present. The cracking differed at the different elongations, and the sample broke after different periods of exposure (*e.g.*, 5–7 minutes); when the sample was on the point of failing, the effective elongation was no doubt less than the nominal value. The ozone absorption increased with increasing strain, and hence the mean ozone concentration was reduced from the nominal value of  $1.0 \times 10^{-3}$  cc. per cc., by amounts differing for different samples, being most reduced when it was most needed; when the reduction in concentration became marked, it was evident which end of the sample had been nearer to the point at which the ozonized oxygen entered. In some cases the rate of cracking was so great that many small pieces fell from the sample and, in cases where the ozone uptake was determined by weighing, these had all to be collected; it is evident that the experimental technique will have to be revised before quantitative work is carried out. Despite these disadvantages, it is concluded that useful results have been obtained, and it should be noted that most of the errors, *i.e.*, presence of unstretched rubber, strains below the nominal value, reduction of ozone concentration, and loss of pieces of cracked rubber, will cause the apparent ozone uptake to be too low.

The results obtained show clearly that the ozone uptake increases markedly with strain, and reaches a limiting value of somewhat less than 0.1 mg. per sq. cm., of unstretched surface per minute, in the region of 100–150 per cent elongation. The best results obtained at present are given below, and are expressed as micrograms ( $\gamma$ ) of ozone per square centimeter of unstretched surface per minute of exposure to an atmosphere containing nominally  $1.0 \times 10^{-3}$  cc., ozone per cc., but having an effective mean value of probably not more than half that figure; it should be remembered that the values are certainly too small.

Percentage elongation	20	40	60	90	100	180	250
Ozone uptake, $\gamma$ /sq. cm. per min.	22	40	48	60	75	88	78

In the case of unstretched rubber, the total uptake after 15 minutes is about  $30\gamma$  per sq. cm.; the oxygen uptake of stretched rubber, in the absence of ozone, was found to be negligible under the conditions used.

At all strains, very severe cracking occurred after exposure for 1 minute, and some cracking was produced by a few seconds' exposure; *i.e.*, unstretched rubber absorbs considerably more ozone than is required to produce cracks in stretched rubber, yet not only does it not crack, but no cracks are produced by subsequent stretching in the absence of ozone, even if this is done as soon as possible after ozonization. The problems thus raised are discussed in Section 6.4.2, but certain aspects of the difference between stretched and unstretched rubber will be considered here. It was shown in Section 5.2.1 that the rate of formation of cracks increases with strain, to reach a limiting value at about 75 per cent elongation, and it is considered that the dependence of ozone absorption on strain is related to this cracking and to the increase in surface area, but not to any change in the reactivity of the stretched molecule. It is suggested that ozone rapidly attacks stretched or unstretched rubber until the thin layer of ozonide is formed which reduces further absorption; in the case of unstretched rubber this stage completes the process, but in stretched rubber cracks are formed also, and these, as they grow, continually expose unattacked rubber. The rate of crack formation and growth increases with increasing strain until the limiting value is reached, and hence it is not

surprising that the ozone absorption should show a similar dependence on strain. When the absorption is calculated on the stretched area, a decrease is found at high strains, but this may be due to excessive reduction of the ozone concentration.

It must be emphasized that, at present, the author believes that this strain-dependence of the rate of crack formation, and hence of ozone attack, is not related to changes in the reactivity of the molecules towards ozone as a result of stressing them, but to the interference with one of the stages in a two-stage process (see Section 6.4.2). Kauzmann and Eyring<sup>76</sup> discuss a similar problem, and appear to reject the view that, during mastication, oxidative attack by oxygen occurs more readily when the rubber is subjected to shearing stresses, and regard the oxygen as interfering with the second stage of a process involving (1) breaking of bonds by mechanical stresses, and (2) the subsequent recombination of the free radicals thus produced<sup>77</sup>. These authors discuss, also, the influence of ozone on mastication of rubber. Kröger<sup>78</sup> claimed that stretched rubber absorbs bromine and iodine more readily than does unstretched rubber, but he gives no details of his experiments, and the present author has not been able to confirm his conclusion. Strips of Mix 270, about 0.5 mm. thick were stretched to different extents and immersed in bromine water, containing 9.5 gm. bromine per liter, for 30 minutes at room temperature. The uptake of bromine was determined by estimating the amount left in the water, and the results, expressed as mg. of bromine per sq. cm. of either stretched or unstretched surface, are given below. The small decrease, with increasing strain, of the uptake per unit stretched surface, may be due to the bromine concentration in the middle of the rubber having risen above zero, owing to the reduced thickness of the sample.

Percentage strain in the rubber	0	14	60	170
Uptake, based on { unstretched surface	6.8	7.3	7.8	9.2
{ stretched surface	6.8	6.8	6.2	5.5

In view of the experiments of Williams and Dale<sup>72</sup>, that the vibrational frequencies of the bonds in rubber are not altered until the strain reaches 400 per cent, it would seem unlikely that low strains could modify the reactivity of the molecules.

### 6.3. INFLUENCE OF THE TYPE OF RUBBER ON OZONE ABSORPTION

In view of the difficulties encountered in measuring large ozone uptakes of stretched rubbers, this aspect of the investigation has been limited to the study of rubbers which are relatively resistant to attack by ozone. Neoprene-GN is remarkably resistant to attack by ozone (see Figure 6*h*), and a sample of Mix 118 stretched 100 per cent was found to absorb only 8 $\gamma$ /sq. cm. per min., *i.e.*, not more than 0.1 of that of natural rubber; comparison of Figures 6*a* and 6*g* suggests that Neoprene is about 20 times more crack resistant than is natural rubber. This resistance is no doubt caused, as suggested by Morgan and Naunton<sup>79</sup> for attack by oxygen, by the proximity of the chlorine atom to the double bond; Noller, Carson, Martin and Hawkins<sup>80</sup> show that chlorine atoms adjacent to the double bond reduce the uptake of ozone by substituted ethylenes, *sum*.-dichlorethylene being almost unreactive.

A sample of vulcanized Thiokol-FA (Mix 149), stretched 100 per cent, gave an absorption of 13 $\gamma$ /sq. cm. per min., i.e., about 60 per cent greater than that

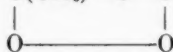
found with Neoprene, while Figure 6*h* shows that this mixing cracks about 50 per cent more readily than does the Neoprene-GN.

Gutta-percha presents an interesting problem: this *trans*-polyisoprene is generally regarded as being much more resistant to attack by ozone than is the *cis*-compound (Hevea rubber), yet it has been shown by Briner and Frank<sup>81</sup> and by Noller, Carson, Martin and Hawkins<sup>80</sup> that *trans*-compounds take up ozone more readily than do the corresponding *cis*-compounds. At room temperature, vulcanized gutta-percha is "frozen", and the molecules do therefore not have sufficient mobility to permit the formation of cracks; for this reason the absorption experiments were performed at elevated temperatures. The vulcanized sample of gutta-percha exhibited marked stress decay at 70° C, and the absorption was therefore measured on unstretched samples. Pieces of mixings 270 and 271 were heated at either 70° C, or 100° C, for about an hour, and then exposed to ozonized oxygen for 10 minutes at the same temperature. At 70° C, both vulcanizates absorbed about 20γ/sq. cm. in the 10 minutes, while at 100° C, Hevea rubber absorbed 23γ/sq. cm., and gutta-percha absorbed 33γ/sq. cm. It is thus evident that gutta-percha absorbs ozone at least as readily as does Hevea rubber, and perhaps more so. The apparent ozone-resistance of gutta-percha and balata is no doubt due to (1) their crystalline state, for example, vulcanized Hevea rubber does not crack when it is "frozen", see Section 4.6.3, and (2) the rapid stress decay associated with these materials at temperatures above the freezing point.

#### 6.4. CONSEQUENCES OF THE REACTION BETWEEN OZONE AND RUBBER

6.4.1. *Information in the literature*—Much work has been carried out on the ozonolysis of rubbers, both natural and synthetic, but the investigators have been concerned more with the constitution of the products of hydrolysis of the ozonides than with the structure of the ozonides themselves; they have, however, obtained clear evidence that ozone normally attacks all the ethylenic linkages and that, at least on hydrolysis, the molecules are broken at these linkages.

Pummerer<sup>82</sup> convinced himself that rubber ozonide contained the structural unit:  $\text{—CH}_2\text{—C}(\text{CH}_3)\text{—O—CH—CH}_2\text{—}$  and, although his reasoning may not



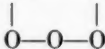
be entirely convincing, there is good reason to believe that this formula is a likely one, as Rieche, Meister, Sauthoff and Pfeiffer<sup>83</sup> have proved that the 2-butene ozonide has the formula  $\text{CH}_3\text{—CH—O—CH—CH}_3$ , the evidence being



based on the products of hydrolysis, the nature of the reactions of the ozonide, various physico-chemical properties, and finally synthesis of the compound by dehydration of dihydroxyethyl peroxide. Long<sup>84</sup> discusses the evidence up to that year, and concludes that this isoözonide structure is correct. It is, however, very unlikely that the isoözonide structure  $>\text{C—O—C}<$  could be built up



from the double bond in one stage, and it seems likely that the primary product had the structure  $>\text{C—C}<$ , as suggested by a number of investigators,



and accepted by Pummerer<sup>85</sup>; although he withdrew his support for its presence

in 1936, it is nevertheless a likely primary product and might have only a transitory existence, being an activated state required by the geometry of the reaction, as in the transition-state theory of Evans and Polyani. Rieche, Meister, Sauthoff and Pfeiffer<sup>83</sup> found that the *cis-trans* isomers, oleic and elaidic acids, produced *cis-trans* isomeric ozonides, showing that the oxygen ring must have been formed in two stages, or rotation would have occurred at the double bond.

6.4.2. *Speculations on the method of crack formation.*—In any speculation on the nature of the ozone attack and on the reason for the formation of the cracks, the main problem is that unstretched rubber can absorb much more ozone than is required to produce cracks in rubber which is stretched during ozonation, and yet no cracks are formed when the rubber is stretched after ozonation. In reviewing the experimental data it is very difficult to avoid the following conclusions:

(1) Macroscopic holes are produced in the vulcanized rubber, and hence primary bonds must be broken.

(2) The cracks are produced only by the simultaneous presence of ozone and strain, and hence this scission of primary bonds must result from the combined effect of ozone and strain on the molecule.

(3) The product of ozone concentration and period of time required to form cracks is constant ( $c \times t$ , see Section 4.5.5), and hence the bond scission must occur almost immediately after attack by the ozone molecule, and before a stable state has been reached; moreover, this bond-scission must be permanent as the effect is cumulative.

(4) If the bond scission occurred at random over the surface, the rubber would merely become oxidized and decrease in molecular weight, but not crack, and hence, at least until the holes reach macroscopic dimensions and can themselves modify the strain-distribution on the surface, some directive influence must be present, causing further scission to occur in the neighboring chains near the point at which the initial scission occurred, *i.e.*, some other effect produces an abnormal reaction and initiates a crack nucleus.

(5) Even at the highest density of protocracks, the cracks are very infrequent compared with the density of ethylenic linkages in the surface, all of which are attacked by the ozone, and hence the type of reaction which leads to breakage of a primary bond is much less frequent than the one which does not break bonds, but, once it has occurred, it appears to be able to perpetuate itself, provided the molecules are still strained.

(6) The strains required to produce cracking are so small that the strain free-energy of the molecule can neither produce scission of primary bonds nor materially affect the rate of chemical attack, hence it would appear more likely that the strain interferes with the second stage of a two-stage process involving (say) chemical fission and subsequent recombination, the strain separating the reactants from one another so that recombination does not occur.

Such a two-stage reaction would appear ready to hand in the form of the primary ozonide-isoözonide transformation discussed in Section 6.4.1, as this occurs in two stages with rearrangement of the atoms during the intermediate stage. It appears unlikely, however, that small strains in the molecule could interfere with this process; moreover, if this reaction is the normal one, it would probably not be that which, in some unknown manner, initiates the nucleus from which a crack is formed. The problem is clearly a difficult one, and the author feels that it is deserving of greater attention from physical chemists.

If, for the purpose of continuing the speculations, a hypothetical two-stage process is postulated in which strain can interfere with the completion of the

second stage, and thus lead to chain scission, and in which this interference occurs only when the strain free-energy exceeds a certain threshold value, some interesting conclusions can be reached. At a given strain, the energy distribution of the molecules will approximately follow the normal distribution function, and there will be a definite probability that a certain proportion will have sufficient energy to prevent the completion of the second stage. If the strain is increased, this proportion will increase, following a normal probit curve (integrated normal probability curve), until substantially all the molecules have the energy required to form the initiation reaction, provided the other, yet unknown, essential factor is also present. If the number of protocracks is simply related to the number of chains broken, as would be the case if the directive influence was effective, then they should themselves follow a probit curve when they are plotted against the strain; the data in Table II (or Figure 13, 3 hours' exposure) have been replotted on linear coördinates as circles in Figure 18, and it can be seen that they appear to fall very close to such a curve (the calculated curve being shown by the dotted line). A straight line could be drawn through the points equally well, but the probit curve is preferred for the following reasons: (1) If the probability of meeting a molecular segment with the requisite energy is 1:1 ( $P = 0.50$ ) at 52 per cent strain, then the probabilities of meeting this amount of energy at lower strains are: 40 per cent strain,  $P = 0.115$ ; 35 per cent, 0.045; 30 per cent, 0.015; 25 per cent, 0.003; 20 per cent, 0.001; 15 per cent, 0.0001; thus for very low strains the probabilities are extremely small. A very approximate check can be obtained for the validity of these low probabilities; from Table II it can be seen that, very approximately, the cracks are first seen at the following strains and periods of exposure: 32 per cent strain, 5 hours; 23 per cent, 9; 21 per cent, 33; 15 per cent, 600 hours, these periods of exposure being in the ratio 1:2:7:120, while the equivalent probabilities are in the inverse ratio 1:8:15:155, the agreement being satisfactory in view of the very incomplete nature of the data in Table II.

(7) A further reason for preferring the probit curve to the straight line exists in the additional data plotted in Figure 13 for strains between 70 and 100 per cent; these are clearly approaching an asymptote in much the same way as does the probit curve in Figure 18, but they have not been replotted in that figure because they do not fit on exactly the same curve. (Figures 13, 14, and 18 were derived from the data in Table II; Figures 15, 16, and 17 were derived from a different sample with a much slower rate of cracking.)

It might be suggested that the data plotted in Figure 18 represent a condition in which very large numbers of molecules are involved, and hence results obtained therefrom would not be applicable to arguments about segments of molecules. It is believed, however, that during conditions of crack growth, and the early stages of coalescence, and before the effects of contiguous cracks modify the opportunities for crack growth, the behavior will be substantially controlled by the scission of individual segments. When crack growth becomes more severe, conditions tend to become stabilized, and the number decreases at higher strains; the curve is then shifted to the left, with a decrease in slope. In Figure 18 the conditions after  $5\frac{1}{4}$  hours' exposure have been plotted on an equivalent scale as crosses, and it can be seen that there is a slight shift to the left and some decrease in slope, but apart from these changes, the calculated line would still represent the conditions reasonably well. If the results for  $8\frac{3}{4}$  hours' exposure are plotted, the shift is appreciably to the left, the mid-point occurring at 46 per cent strain, instead of 49 per cent for the  $5\frac{1}{4}$ -hour

data, and 52 per cent for the  $2\frac{3}{4}$ -hour data; these other results thus support the view that Figure 18 could represent conditions applied to molecular segments.

6.4.3. *Other theories of crack formation*—Kearsley<sup>43</sup> stated that "The very low tensile strength of the film produced by ozone on the surface of the rubber under tension apparently offers the best explanation of the cracking phenomena associated with it", and Tuley<sup>65</sup> states that the reaction product of ozone with rubber is a viscous liquid lacking in physical strength, and therefore unable to withstand a stress. Both of these authors either make the assumption that

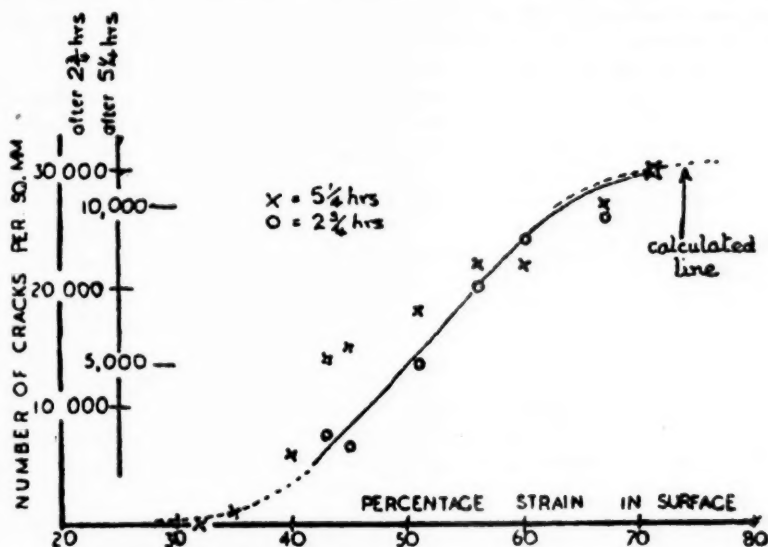


FIG. 18.—Relation between surface strain and number of cracks per sq. mm.

ozone does not attack unstretched rubber, or else they have failed to realize that, on their theories, ozonized and unstretched rubber should crack, or at least show a fall in tensile strength, on being strained; this does not occur.

## DISCUSSION OF METHODS OF PREVENTING CRACKING

### 7.1. PRACTICAL ASPECTS OF THE CONCLUSIONS REACHED

Cracking is produced by the action of ozone on the surface of stretched rubber. Unstretched rubber absorbs ozone until a film of ozonide is built up sufficiently thick to reduce further absorption, but no cracks are produced; this ozonized layer is very thin, and is not readily detected. The reaction must, therefore, be limited to the surface layers, and it appears that any changes in compounding which affect only the body of the rubber are unlikely to improve the resistance to cracking. This would explain why antioxidants and mineral fillers do not influence the rate of cracking, except in so far as they modify the rate of formation of an oxidized (not ozonized) surface skin.

It is clear that ozone attack on rubber is more widespread than was formerly realized, and much of the behavior previously attributed to sunlight is now shown to be due to ozone. Ozone thus takes its place with oxygen, heat, light

and oils as agents which produce important deterioration in vulcanized rubber, while a number of materials, notably rubber tubing, fail in service solely as a result of ozone attack. The bulk of rubber is used for the manufacture of tires, which are subject to exposure-cracking, and it has been suggested, *e.g.*, by Eccher<sup>6</sup>, that flex-cracking is due, at least in part, to ozone attack, although this subject is at present controversial. From the point of view of more concentrated ozone, the increasing use of this gas in the purification of air and water may lead to problems in the life of rubber goods employed in these connections; for example, pipe jointing rings are used under compression. It may not be inappropriate to point out here that failures in stretched insulating tape have been responsible for several deaths<sup>86</sup>.

It is thus evident that the role played by ozone must be reconsidered, and it is possible that ozone may be as important as oxygen in oxidizing rubber. In this connection Briner and Perrottet<sup>87</sup> claim that ozone is not entirely removed from air until it is heated to 800° C, and that air so treated does not produce many of the reactions previously attributed to autoxidation, for example aldehydes are not autoxidized in this atmosphere.

## 7.2. METHODS OF PREVENTING EXPOSURE-CRACKING

The characteristic cracking is produced only when both strain (stress) and ozone are present, so that the removal of one of these factors prevents the attack.

Cable-makers, who may need to combat the fair concentrations of ozone produced by corona, approach the problem from the point of view of removal of stress, by heating the cable after installation or by using compounds containing large quantities of materials, such as bitumens, which increase the rate of stress decay, while designers of tire-treads endeavor to control stress-distribution to avoid relatively high values of strain.

The second method of combating cracking would be to prevent the ozone from reaching the rubber, and it was shown in Section 7.1 that the most fruitful method of approach would be by means of surface treatments, rather than by modifications to the interior of the rubber.

A well-known method of producing surface protection is the incorporation in the compound of waxes which bloom on to the surface, and this method was first advocated in a German patent in 1881<sup>88</sup>. These waxes assist in preventing attack by low concentrations of ozone, presumably by forming a physical barrier to diffusion of the gas. Use of these waxes can be one of the most valuable methods of providing protection, but their several limitations must be realized. These are:

(1) Waxes are not protective against the higher concentrations of ozone; for example, Garvey and Emmett<sup>14</sup> noted that refined paraffin wax gave improved ozone resistance to Hycar OR-15 and Hycar OR-25, but no protection was provided if the ozone concentration was too high, and Van Rossem and Talen<sup>1</sup> found that air containing  $3 \times 10^{-5}$  cc. per cc. of ozone brought about a very distinct formation of cracks in 30 minutes on a vulcanizate containing paraffin wax. Somerville, Ball, and Cope<sup>69</sup> found that the addition of 1 per cent of paraffin wax to the mixing permitted bad deterioration in ozonized air, but provided protection in sunlight, and they say "Possibly this might be explained by the protective film of paraffin breaking under stretch, but uniting again during the period of sunlight aging when the weather was fairly hot." The present author would remark that the surface of tire-tread vulcanizates

can become relatively hot when insolated and he has watched, through a low-power microscope, the flakes of a badly-cracked paraffin wax bloom melting and running over the surface when exposed to hot autumn sunshine. Another reason for the poor protection provided against higher concentrations of ozone lies in the relative inelasticity of the wax skin; if some ozone penetrates the wax film and forms a crack in the rubber, the local disturbance of surface strain is likely to crack the layer of wax, thus permitting further rapid attack, and this process would occur more rapidly in higher concentrations of ozone.

(2) Northam<sup>53</sup> points out that bloom may be cracked easily by further stretching, or by flexing. The present author has noted a characteristic of waxes which provide good protection and which overcomes this fault; one of these waxes, Okerin 333, can be incorporated in rubber in very large proportions, and provides protection against exposure-cracking when used in concentrations ranging from 2 to at least 30 parts per 100 parts of rubber yet it does not show a pronounced bloom. If paraffin wax is used, however, proportions of 5 parts or higher produce a very heavy bloom which can be scraped off easily, and will readily crack into flakes which scatter the light and produce the whitening of the surface which is seen when the sample is bent sharply. It is possible that the superior protection provided by the Okerin wax may lie in a capacity continually to rebloom to the surface and repair damage which occurs to the film.

In this connection, Garvey and Emmett<sup>14</sup> say "Protection by means of oils, beside being dependent upon the chemical nature of the material, appear to be a function of viscosity and/or the rate of replacement at the surface. Materials which can quickly migrate to the surface to replace weathered or damaged films are more satisfactory than viscous oils with slow bleeding rates."

(3) It should be noted that any tendency for a pinhole or small crack to develop at high strains leads to a very rapid failure of the sample, as was found with carnauba wax (see Sections 3.4 and 5.3.3), and the final result may be much worse than that found in the unprotected sample.

Other workers have suggested different types of protective films; for example, Williams<sup>3</sup> obtained reduced cracking by oxidizing the surface of the sample with copper salts, and Haushalter<sup>16</sup> noted that a complete film of cellulose provided protection.

Another very successful method of providing surface protection has been to employ a flexible protective paint on the surface; this type of paint is usually prepared from bitumens<sup>89</sup>, and may contain antioxidants and light-absorbent dyes<sup>90</sup>; such a paint has provided protection against a concentration of ozonized oxygen containing  $1.0 \times 10^{-3}$  cc. per cc. ozone for 15 minutes without any sign of cracking of the rubber when the paint was washed off. These paints can contain rubber, which should be excessively masticated or peptized so that stress decay may be as rapid as possible and the film may thus itself remain free from strain, although it can follow changes of strain in the vulcanized substratum. Tuley<sup>65</sup> found that primary diarylamines, especially 4,4'-diaminodiphenylmethane, gave protection against "frosting" produced by ozone, and such antioxidants may find application in protective paints. In using the paints, the article should first be stressed to the normal extent and then painted with at least two coats; if this is not done, pinholing may result, with the consequent series of effects described in Section 5.3.3, and some of the disappointments found with these paints may be due to this cause.

A more fundamental method of preventing ozone attack would be to remove the ethylenic linkages on the surface without destroying the rubbery

properties. Some progress has been made along these lines, for example bromine adds to the double bond, but the resulting product is hard and relatively inelastic. If bromination is carried out on unstretched rubber, no protection is obtained because the film breaks on stretching, but if bromination is carried out on stretched samples, some protection against ozone attack may be afforded. The ideal method of preventing attack by ozone would be to avoid the introduction of polar atoms, such as bromine and oxygen, and to hydrogenate the double bonds.

### SUMMARY

"Exposure-cracking" is the fissuring which occurs when stretched rubber is placed in an atmosphere containing ozone, and is frequently wrongly described as "sun-cracking". These cracks form in the rubber at right angles to the applied stress and must be distinguished from crazing, the fissures of which occur in an oxidized surface layer and may run in any direction.

It is shown that there is a "critical elongation" at which cracking is maximal, but that the relation between the severity of cracking and the surface strain can be greatly modified by changes in the compounding ingredients. Butadiene type of rubbers do not differ greatly in resistance to exposure-cracking, whereas the Neoprene types and Thiokol-FA possess marked resistance.

The only factors essential for the production of exposure-cracking are ozone and strain in the sample, and sufficient ozone must be present in the atmosphere to produce the deterioration observed. Light is not only unnecessary, but actually has a retarding effect on the production of cracks.

Three different phenomena must be carefully distinguished (1) the rate of ozone attack; (2) the rate of formation of cracks; and (3) the rate of growth of cracks. The rate of formation of cracks increases with increase of strain until a maximum is reached at about 75 per cent elongation, but the mean rate of growth of cracks is most rapid at 20 per cent elongation because the surface strain is most persistent at this elongation. The actual growth of cracks has been studied microscopically, and it is shown that large cracks are formed by the coalescence of small cracks, and the collapse of neighboring ones.

The rate of ozone absorption is considered, and speculations are advanced to explain the formation of cracks and their greater incidence at high strains. The course of ozone attack indicates that there is little likelihood of producing improvement in resistance by altering compounding ingredients such as fillers and antioxidants, and confirms that the most efficient methods will be based on some type of surface protection.

### ACKNOWLEDGMENTS

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# APPENDIX

## COMPOSITION OF MIXING USED

Mix No.	Type of elastomer	Type and amount of fillers	Pine tar	Stearic acid	Zinc oxide	Sulfur	Accelerators	Other ingredients
							MBT	DPG
1	Natural rubber	EPC, 50	4.5	2.5	5	3	0.8	—
2	GR-S	EPC, 50	3	1	3	2	1.0	0.25
3	Buna-85	EPC, 50	2	2	5	1.5	1.0	0.25
4	Hycar-EP	EPC, 50	3	2	3	1.75	1.0	0.25
52	GR-S	Whiting, 105	—	1	5	2	1.0	0.25
53	GR-S	Silene, 91	—	1	5	2	1.0	0.25
54	GR-S	C. Clay, 105	—	1	5	2	1.0	0.25
86	GR-S	AW, 70; Sl, 30	—	0.5	3	2.5	MBTS	PAE-3 (2292), 30
87	GR-S	AW, 70; Sl, 30	—	0.5	3	2.5	1.0	PAE-3 (2292), 30 MPC, 5
98	Perbunan	EPC, 50	—	0.5	5	1.5	1.5	DBP, 10
99	Perbunan	MPC, 45	3	2	5	2.5	1.0	—
101	Perbunan	Mag. carb., 65	3	2	5	2.5	1.0	—
103	Perbunan	French C, 80	3	2	5	2.5	1.0	—
107	Hycar-OR	EPC, 50	—	0.5	5	1.5	1.5	DBP, 10
110	Hycar-OR	Mag. carb., 65	3	2	5	2.5	1.0	—
111	Hycar-OR	C. clay, 80	3	2	5	2.5	1.0	—
112	Hycar-OR	French C, 80	3	2	5	2.5	1.0	—
118	Neoprene-GN	EPC, 40	—	2.5	1	1	—	Anti-oxidant, 2; MgO, 4
119	Neoprene-GN	EPC, 40	—	2.5	1	—	—	TCP, 2.5; MgO, 4
149	Thiokol-FA	MT, 45	—	0.5	10	—	0.35	DPG 0.1

## APPENDIX—Continued

Mix No.	Type of elastomer	Type and amount of fillers	Pine tar	Stearic acid	Zinc oxide	Sulfur	Accelerators	Other ingredients
170	GR-S	EPC, 50	—	1	3	2	MBT 1.0	Paraffin wax, 0
172	GR-S	EPC, 50	—	1	3	2	1.0	Paraffin wax, 1
173	GR-S	EPC, 50	—	1	3	2	1.0	Paraffin wax, 2
174	GR-S	EPC, 50	—	1	3	2	1.0	Paraffin wax, 5
181	GR-S	EPC, 50	—	1	3	2	1.0	Carnauba wax 5
270	Pale crepe	—	—	0.5	0.5	2	Butyl Zimate, 0.5	—
271	Gutta-percha (purified)	—	—	—	5	3	DPG 1	—

## Abbreviations used:

AW	Activated whitening
C. Clay	Colloidal china clay
DBP	Dibutyl phthalate
DPG	Diphenylguanidine
EPC	Easy-processing channel black
French C	French chalk
Mag. carb.	Magnesium carbonate
MBT	Mercaptobenzothiazole
MBTS	Dibenzthiazyl disulfide
MgO	Magnesium oxide
MPC	Medium-processing channel black
MT	Medium thermal black
PAE-x(y)	Pool aromatic extract (Group x, Type y)
SL	Silene
TCP	Tricresyl phosphate
TET	Tetraethylthiuram disulfide

Mix 270 is the transparent mixing.

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# RETRACTION AND STRESS PROPAGATION IN NATURAL AND SYNTHETIC GUM AND TREAD STOCKS \*

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## INTRODUCTION

Natural and synthetic rubbers (elastomers) are characterized by their long-range reversible elasticity. More particularly, the existence of a retractive force distinguishes rubbers from materials like beeswax, which may be extended but do not snap back.

Whereas all rubbers show a snapback, the good rubbers show a fast snapback. Thus the speed of snapback is an outstanding index to the quality of the rubber. For instance, both Hevea and Butyl show snapback, but Butyl snaps back much more slowly than Hevea. This is the reason for the poor rebound in Butyl. Incidentally, the speed of snapback may be, and actually is, used as a simple "hand test" for progress of cure. One bends a cured sheet and observes how fast it straightens out again. In this example the speed of recovery after bending is observed. The speed of snapback may be studied, of course, for any deformation: bending, torsion, shear, compression, extension, etc. Since stress-strain data are used so extensively in rubber technology, snapback after extension was studied first. Snapback will be used in this restricted sense in the following text.

Besides characterizing the quality of a polymer, the speed of snapback is of great direct importance for tire construction. Sluggish snapback may lead to increased flexing, *i.e.*, increased heat generation. In addition, slow snapback means less grip of the tire on the road, assuming equal wetting conditions.

## EXPERIMENTAL METHOD

### STYLUS ON RECORDING DRUM

The speed of snapback can be obtained if the change of length with time of a freely retracting rubber bar can be recorded. The speed of snapback may be obtained by taking the slopes of the length *vs.* time curves. The upper limit for the velocity of the tip of a freely retracting natural rubber band was calculated to be larger than 200 miles per hour (9000 cm. per sec.) at 450 per cent elongation. Therefore the whole snapback must take place in a time interval of the order of 10 milliseconds or less. Recognizing these facts, an obvious method of recording the length-time curve is high-speed photography as perfected by Edgerton. The photographic method will be discussed later in this paper.

In the apparatus used, the rubber sample was clamped at one end. A light

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stylus was fastened to the other end. The stylus was connected with a light frame, which was kept in a straight line during its motion by two guide-wires. The weight of the frame and stylus was less than one gram. The weight of the rubber bar of  $\frac{1}{4}$  inch-square cross-section and 10-inch length was about 10 grams. The motion of the stylus during the retraction of the sample was recorded on a revolving smoked drum (25 inches in circumference and 20 inches in length), which was driven by a synchronous motor at 1800 r.p.m. Thus a record of the length-time curves was obtained for the determination of the slopes and recognition of details.

#### INFLUENCE OF STYLUS

To study the influence of the weight of the stylus (and of the weight of the unstretched rubber in the grip), weights of increasing size were attached to the stylus to permit an extrapolation to zero weight. In Figure 1 the maximum

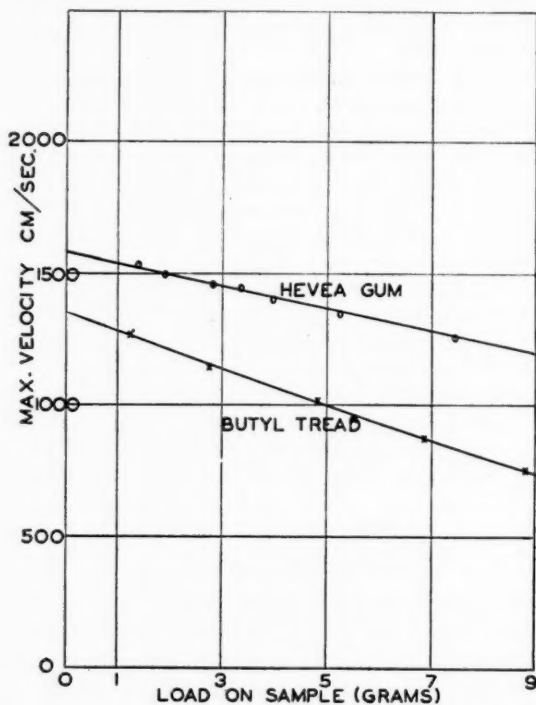


Fig. 1.

velocity of the tip is plotted against the weight for the two extreme cases of Hevea gum and Butyl tread for 50 per cent initial elongation. Straight lines were obtained for both stocks within the experimental accuracy. This fact permits a simple extrapolation. The first point on each of the curves represents the velocity with the stylus and the unstretched rubber, but without any additional weight. The extrapolated velocities are about 3.5 and 6 per cent higher than the original values for Hevea gum and Butyl tread, respectively.

## RESULTS BY STYLUS METHOD

Hevea, GR-S, and GR-I gum and tread stocks were investigated<sup>1</sup>. For Hevea and GR-S, gum and tread stocks differ only in that the tread stocks contain carbon black, and the gum stocks contain a softener. Butyl tread is obtained from the gum stock by the addition of mercaptobenzothiazole and carbon black. The cures were optimum, based on maximum tensile strength tests.

Figure 2 gives the elongation as a function of the time for four different elongations. The duration of the snapback increases from about 7 to 10

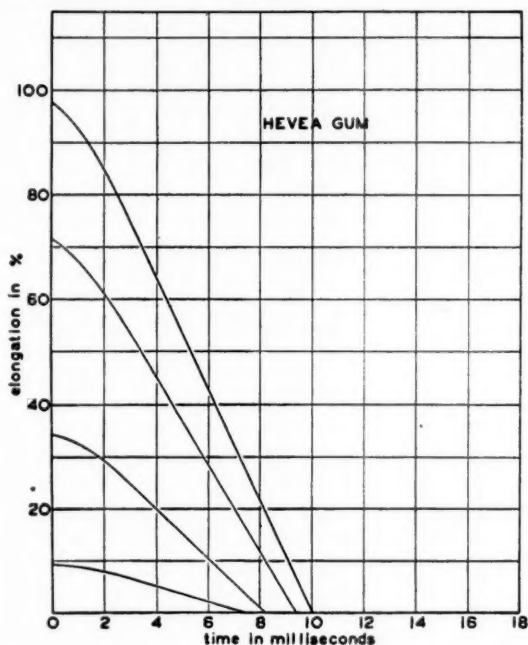


FIG. 2.

milliseconds for the range of elongations covered. All these elongation curves meet the time axis, without showing inflexion points. Figure 3 represents the negative of the slopes of the two lowest elongation curves, plotted against the successive elongations on retraction (velocity curves). These slopes were not taken from Figure 2, but directly from the original records so as to obtain greater accuracy. For the upper curve it took about one-third of the initial elongation (and a third of the duration as Figure 2 shows) to attain the final maximum velocity represented by the horizontal line. The straightness of that line indicates that the final maximum velocity, once attained, will persist over the rest of the retraction.

Figure 4 shows a surprising and important result, which was obtained to check theoretical considerations outlined in Part VI. In Figure 4, the actual change in length of the sample is plotted against the time. The top curve describes the path of the tip of the sample and is, of course, almost identical with the top curve of Figure 2. The sample in Figure 4 was only half as long

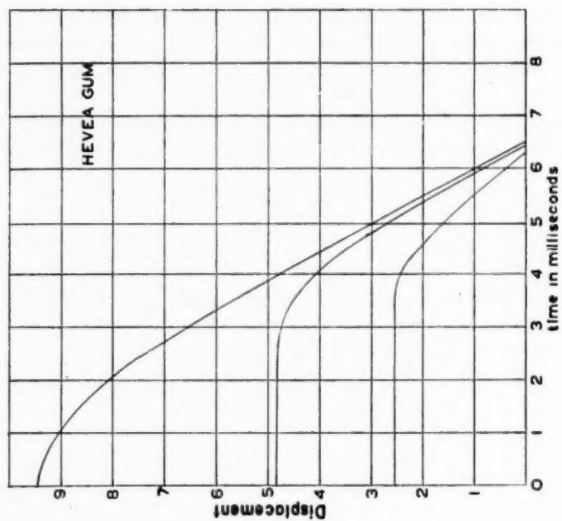


Fig. 4.

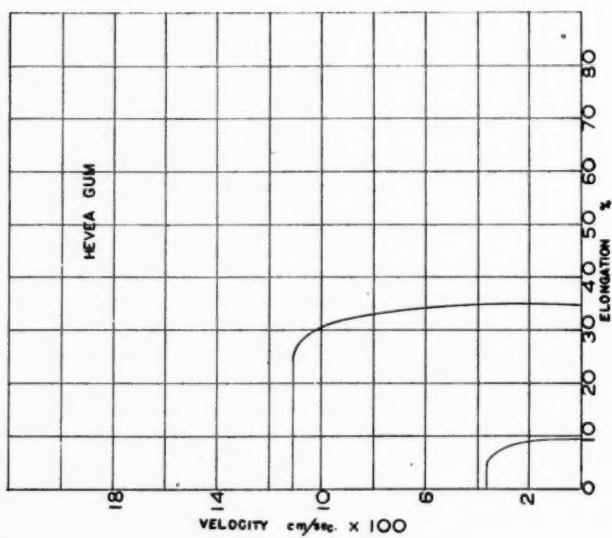


Fig. 3.

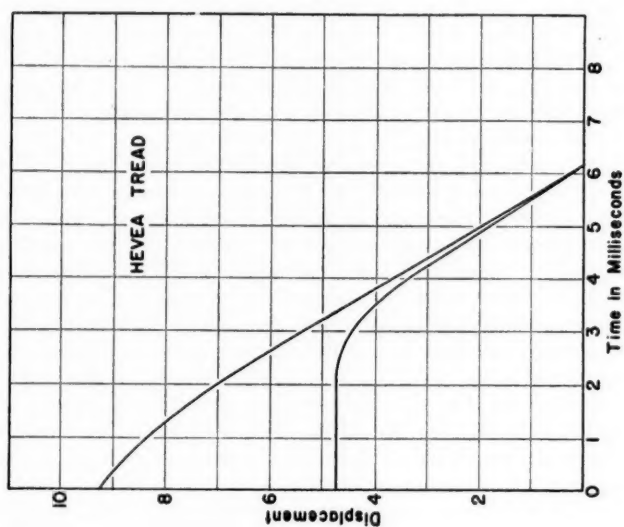


Fig. 6.

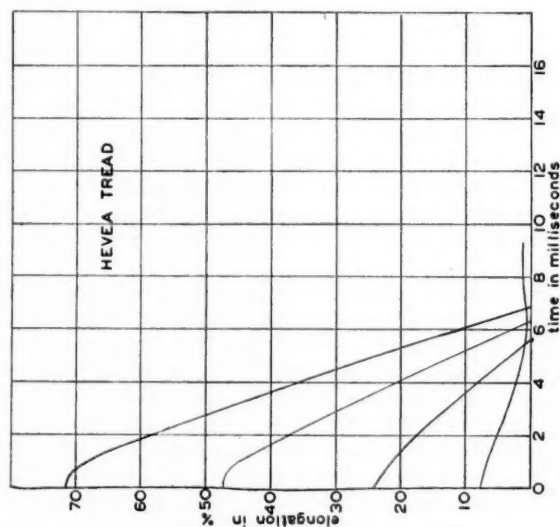


Fig. 5.

as that of Figure 2. This accounts for the longer duration in Figure 2. The middle curve describes the retraction of the middle of the bar and shows quite a different behavior. The middle of the bar starts to move only after the first half has retracted. The lower curve describes the motion of an element at a quarter-length position. Again it lags behind the end, and somewhat behind the middle. The final maximum velocity of the middle is only slightly smaller than that of the tip, and only slightly larger than that of the quarter. The top and middle curves were obtained by fastening a stylus to the tip and another one to the middle of the bar.

Figure 5 shows elongation curves for the Hevea tread stock. Whereas the three upper curves show qualitatively the same behavior, the bottom curve shows two new effects. First, it does not go to zero, but to a minimum. This indicates a permanent or a temporary set. Secondly, after reaching a minimum, it rises again. This rise may be ascribed to the compression of the bar.

Figure 6 shows a two-stylus run (one at the tip and one at the middle of the sample) with essentially the same results as for the gum stock; cf. Figure 4. It should be pointed out that in the three upper curves of Figure 5 this tread stock showed an inflection point which is not indicated on the scale of Figures 5 and 6. Consequently, the velocity curve for any of these upper curves would show a dip at the velocity axis, similar to that of Figure 11 for GR-S tread, but the dip would be much smaller. The dip is visible, of course, for the bottom curve of Figure 5.

Figure 7 gives the elongation curves for a GR-S gum stock. The bottom curve (for the lowest elongation used) is similar to the bottom curve for Hevea tread in Figure 5. Here the set is quite pronounced, and slows the sample up before it buckles. One notices that GR-S gum needs about twice as long to snap back as Hevea gum.

Figure 8 shows the velocity curve with a dip corresponding to the S-shape of the elongation curves.

Figure 9 gives the results of a two-stylus run. Just as for Hevea, the middle of the bar exhibits a delayed snapback.

Figure 10 gives the elongation curves for a GR-S tread stock. The two lowest curves show damped vibrations more developed than for Hevea tread or for GR-S gum. The three upper curves have the same character as the corresponding elongation curves for Hevea tread (cf. Figure 5) and reveal the remarkable speeding up of the snapback of GR-S by carbon black reinforcement.

Figure 11 shows a velocity curve with a single dip caused by the single inflection point.

Figure 12 shows the result of a two-stylus experiment. Again the middle is delayed and moves only with a slightly smaller velocity than the tip of the bar.

Figure 13 shows elongation curves for a Butyl gum stock. All curves show a single S-shape (single inflection point). Even at the lowest elongation used, overdamping is apparent in the last half of the elongation curve.

Figure 14 exhibits a velocity curve with a single dip, like in Figure 11 for GR-S tread, caused by the single inflection point in the elongation curves.

Figure 15 represents elongation curves for a Butyl tread stock. Except for the higher elongation used, all the curves show the inflection point very markedly, *i.e.*, are strongly overdamped. The lower elongation curves reveal considerable temporary or permanent set.

Figure 16 shows a velocity curve. Because of the strong damping the final velocity is not only smaller than the maximum velocity, but goes to zero, as an almost linear function of the elongation.

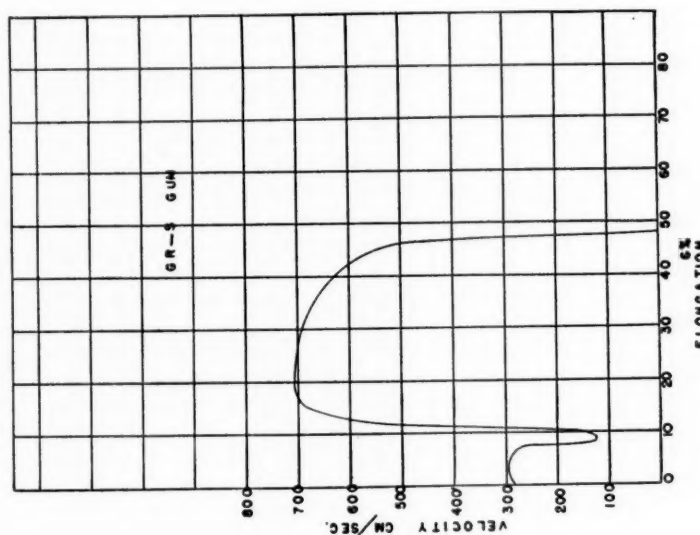


FIG. 8.

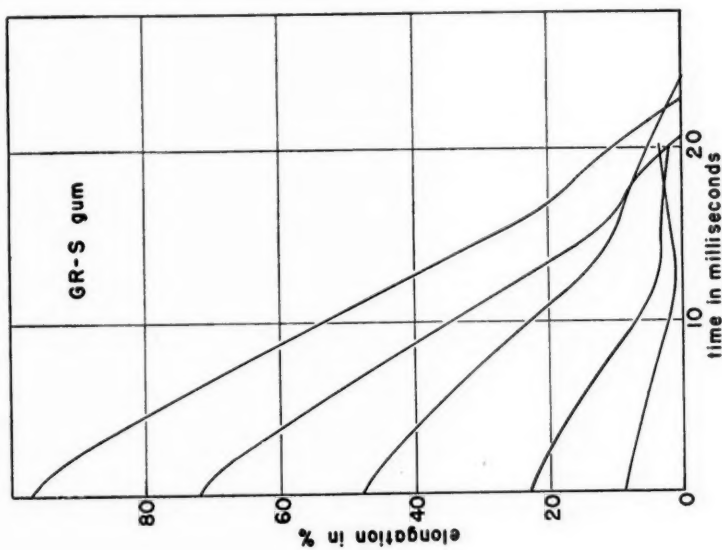


FIG. 7.

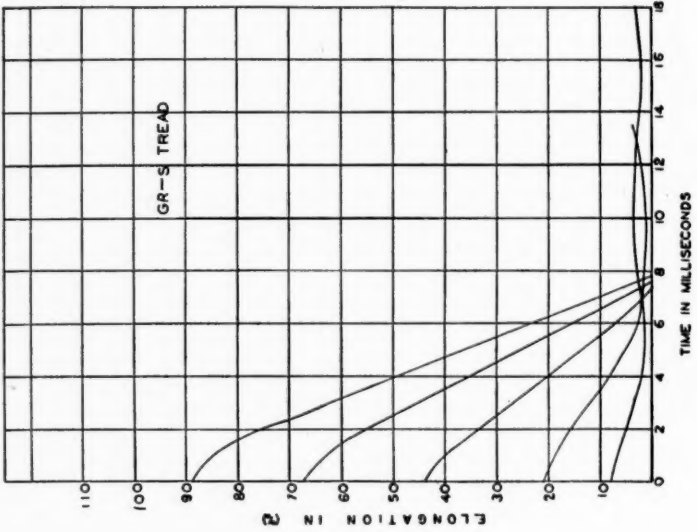


Fig. 10.

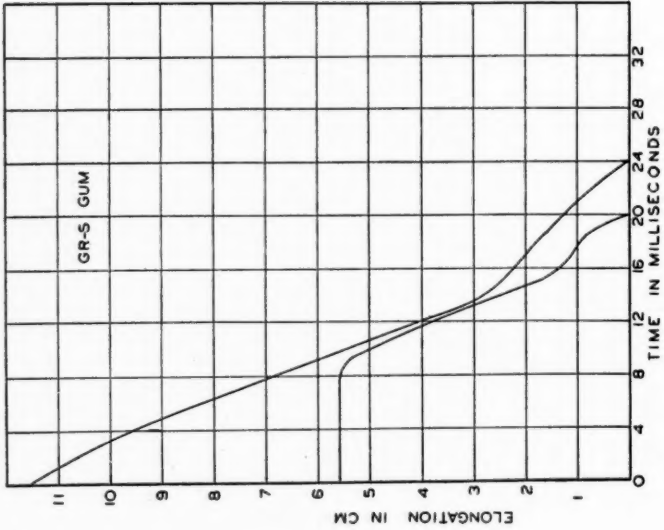


Fig. 9.

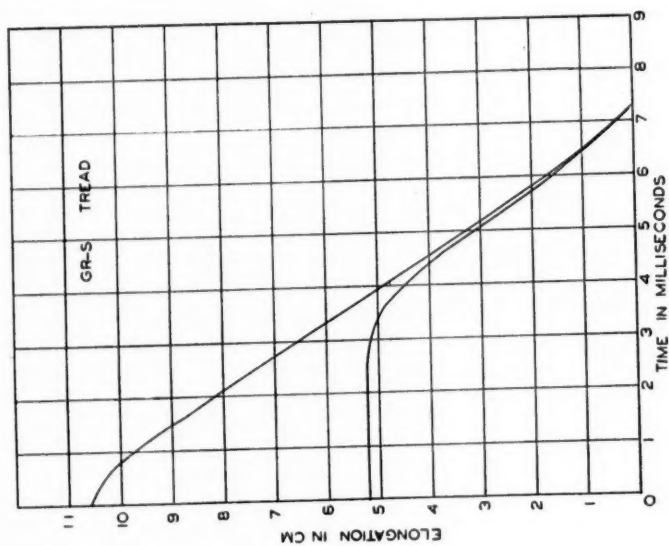


Fig. 12.

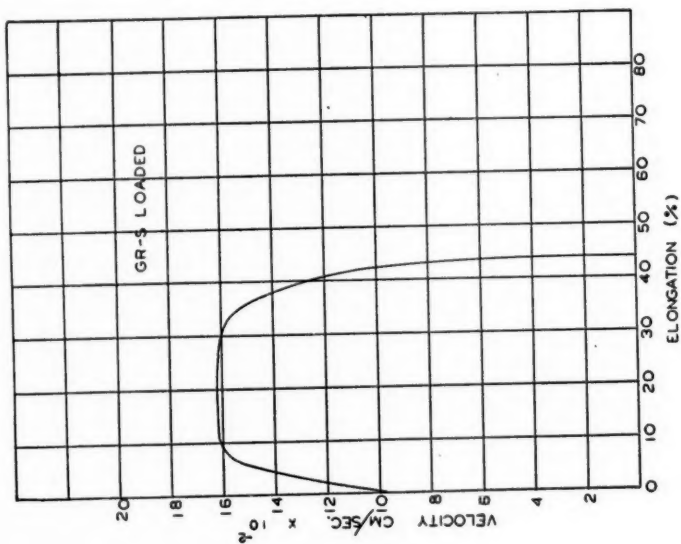


Fig. 11.

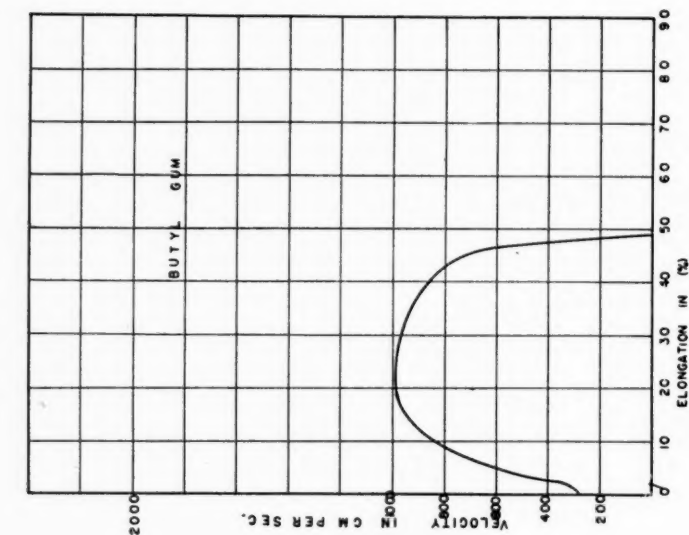


FIG. 14.

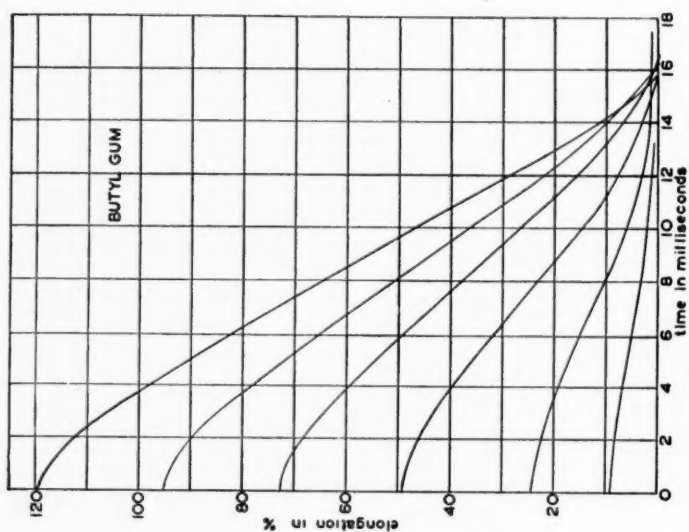


FIG. 13.

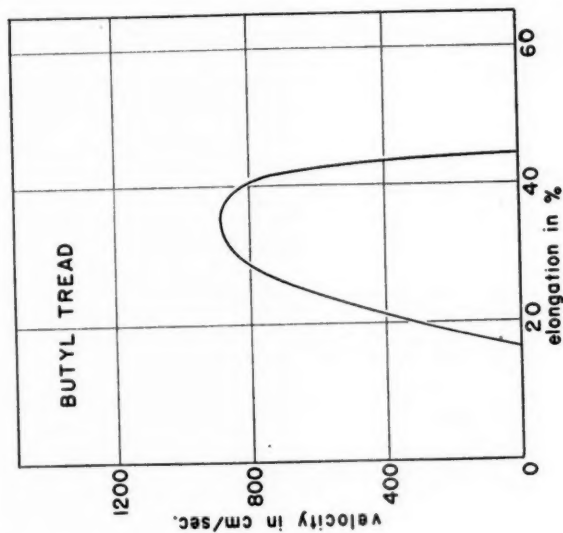


Fig. 16.

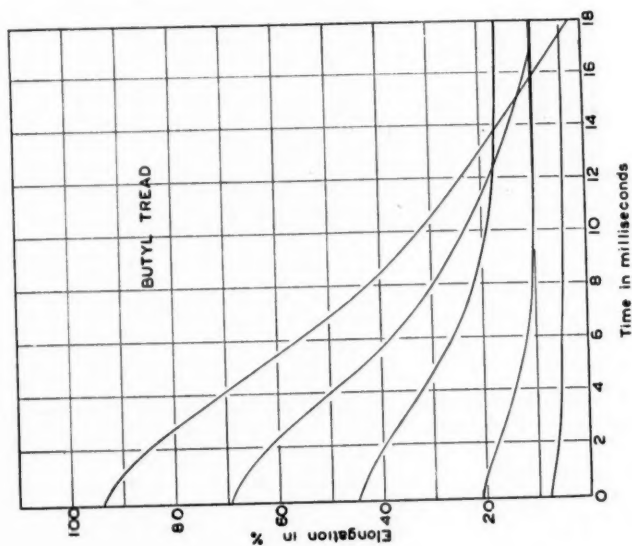


Fig. 15.

Figures 17 and 18 show the maximum velocities plotted against initial elongation for Hevea gum, Butyl gum and tread. Butyl tread, while very sluggish at lower extensions, catches up with Hevea gum above 200 per cent; GR-S gum without softener<sup>2</sup> is much more snappy than one containing Bardol-B. Another noteworthy feature is the crossing of the Hevea tread curve

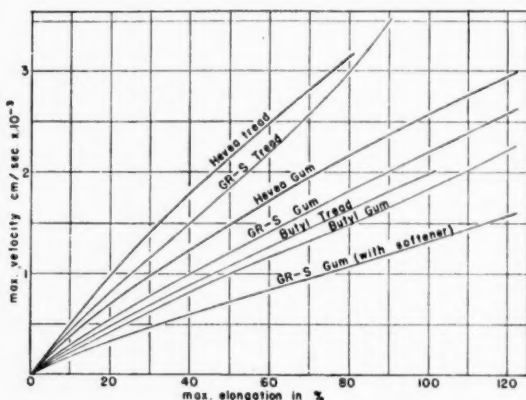


FIG. 17.

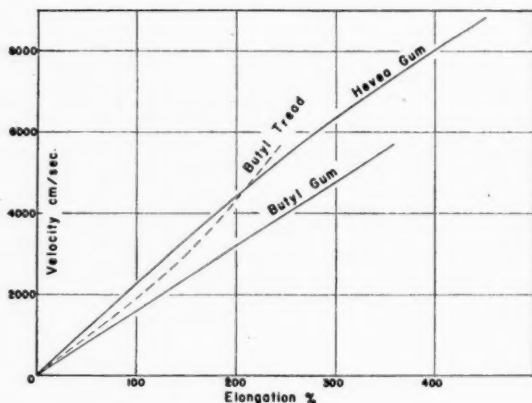


FIG. 18.

by the GR-S tread curve. However, at lower elongations (the range important for tires), Hevea is superior to GR-S.

#### PHOTOGRAPHIC STUDY OF THE RETRACTION PROCESS

Instantaneous photographs<sup>3</sup> of the retraction were taken by an ordinary camera in the illumination of a stroboscopic lamp (strobolux). This simple method (strobolux photography), however, does not provide a time scale, and therefore had to be supplemented by the use of Edgerton high-speed photography method.

Figure 19 shows a set of instantaneous photos of Hevea gum at different

stages (elongations) of the snapback. The initial elongation was 100 per cent. One sees very clearly the wave pulse progressing along the sample. The white dots are equidistant at the start of the retraction, and their separation indicates the progressive retraction of the sample. In Hevea tread the wave pulse is visible, but is less sharp than in the case of Hevea gum. This diffuseness is caused by the larger internal friction of the tread stock compared with the gum stock. Some buckling takes place in the last phase of the retraction, in accordance with the elongation-time curves of Figure 6.

Figure 20 shows a set of instantaneous photographs of GR-S. The moving pulse is still visible, but is more diffuse than for the Hevea tread. The GR-S tread shows a behavior similar to that of Hevea tread. This similarity of the tread stocks is well known from other data. The wave pulse is more diffuse for GR-S because of its larger internal friction.



FIG. 19.

Figure 21 exhibits the snap of Butyl gum and tread, and their sluggish character. The wave pulse is too diffuse to be seen. In addition, the retraction is slowed down so much by internal friction that the pulse arrives at the fixed end before the sample is completely contracted.

In principle, most of the information which can be obtained from smoked-drum records could be derived from timed high speed movies which we took (the time was recorded on the film by a spark at 1/120-second intervals). The motion of the tip as a function of the time may be plotted, *i.e.*, the elongation-time curves. Also, from the same photographs, the motion of any point behind the tip as a function of the time may be obtained, corresponding to the results of the two-stylus experiments. The accuracy depends on the sharpness of the system of marks (dots or lines) put on the sample to indicate the element positions.

From the instantaneous photographs alone, without knowing the time of retraction (which we could take from the elongation-time curves), one could plot the extension of each element (differential extension) as a function of the

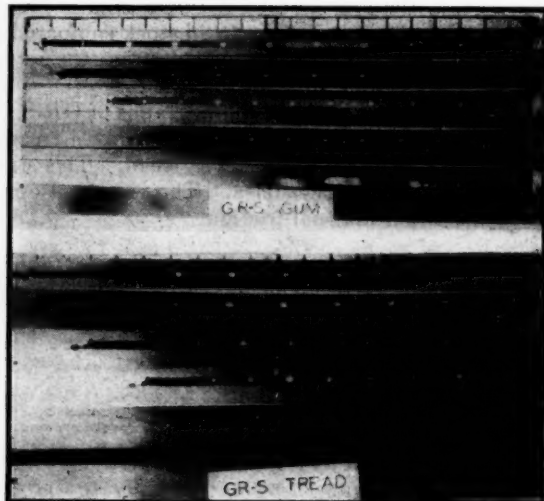


FIG. 20.

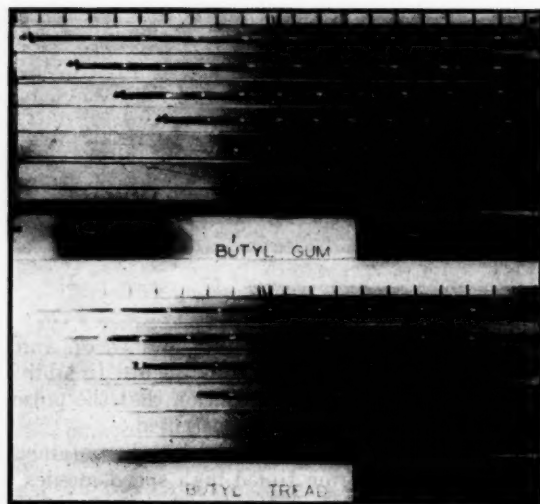


FIG. 21.

distance from the fixed end. This was done in Figure 22 for Hevea gum and for Butyl tread at two different times. These curves show what we know already from the photographs, namely, the motion of a comparatively sharp wave pulse or "necking" for Hevea gum and of a quite diffuse pulse for Butyl tread.

We notice that increasing time shifts the curve for Hevea gum parallel to the ordinate axis, but the shift is parallel to the abscissa axis for Butyl tread.

### DISCUSSION AND EXPLANATION OF THE RESULTS

A theory of the retraction of rubber has been developed by James and Guth<sup>4</sup> and the results are as follows:

We consider a uniform elastic rod of length  $l_0$  fixed at one end, with linear density  $\rho$  in the unstretched state. We assume that Hooke's law holds, with Young's modulus  $E$ , and that frictional forces are proportional to the rate of deformation. Let  $x$  be a measure of distance in the material of the unstretched rod, starting at the fixed end, and let  $u(x)$  be the displacement of the material corresponding to the indicated value of  $x$ . In the absence of body forces, the behavior of the rod in extension and retraction is governed by the wave equation:

$$\rho \frac{\partial^2 u}{\partial t^2} = f \frac{\partial^3 u}{\partial x^2 \partial t} + E \frac{\partial^2 u}{\partial x^2} \quad (1)$$

If the rod is initially uniformly stretched with fractional extension  $\epsilon$ , and is

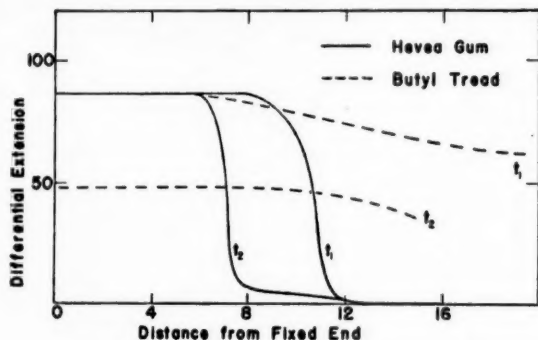


FIG. 22.

released at time  $t = 0$ , the boundary conditions are:

$$\begin{aligned} \frac{\partial u}{\partial x} &= \epsilon, & \frac{\partial u}{\partial t} &= 0 & \text{for all } x \text{ at } t &= 0 \\ u &= 0 & & & \text{for all } t \text{ at } x &= 0 \\ f \frac{\partial^2 u}{\partial x \partial t} + E \frac{\partial u}{\partial x} &= 0 & & & \text{for } x = l_0 \text{ when } t > 0 \end{aligned} \quad (2)$$

In the limiting case of small friction,  $f = 0$ , the solution becomes, with  $v = (E/\rho)^{1/2}$ :

$$\begin{aligned} u(x, t) &= \epsilon x & l_0 - x > vt \\ u(x, t) &= \epsilon(l_0 - vt) & l_0 - x < vt < l_0 \end{aligned} \quad (3)$$

According to this solution a pulse of acceleration arises at the free end at the moment it is released, and travels, with respect to the unstretched material, at a rate  $v$ ; its rate of transmission in space is  $v_p = (\epsilon + 1)v$ . Each portion of the bar is stationary until it is reached by this pulse. The velocity of the tip of the bar is  $v_t = -\partial u / \partial t = \epsilon v$ . As the pulse passes over it the stress is completely relaxed, and the material reaches its final velocity  $\epsilon v$ . When the acceleration pulse reaches the fixed end of the material, after time  $t_c = l_0/v$ ,

the bar is unstretched and in uniform motion at the rate  $\epsilon v$ , the original potential energy is completely converted into kinetic energy. After this time a solution other than Equation (3) begins to apply. The wave pulse is reflected at the fixed end, and a pulse of deceleration begins to progress back down the bar. In the case of a rod in which transverse motion is not prevented, as in the case of a retracting rubber band, buckling begins at the moment of reflection of the pulse.

This motion is shown schematically in Figure 23. This plot shows the change in the position of various points on the sample during the time of retraction. The tip of the sample travels in a straight line from  $l$  to  $l_0$ . In the same time the wave pulse travels from  $l$  to 0, *i.e.*, the entire length of the sample. Any point on the sample between 0 and  $l$ , such as  $l/2$  or  $l/4$ , does not change

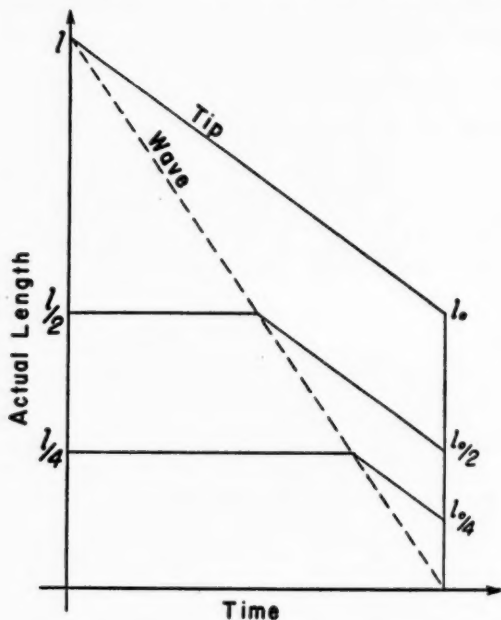


FIG. 23.

position until the wave pulse arrives at that point. Then it acquires the same velocity as the tip, and travels with this velocity until the sample has completely retracted. After the sample has completely retracted it, of course, buckles, beginning at the fixed end.

If we plot this same motion, using the displacement or extension instead of the actual length, we get the graph seen in Figure 24, for the tip and for any point behind the tip. From Figure 24 it follows that the velocity-extension curve is simply a rectangle.

The first element has zero mass. Applying a finite tension, an infinite acceleration results—the final velocity is attained instantly. This is in contrast to the free vibration of a concentrated mass, which always starts with zero velocity. For the actual stylus experiments (*cf.* Figures 2 and 3) the velocity starts with zero. This is caused by the weight of the stylus and of the

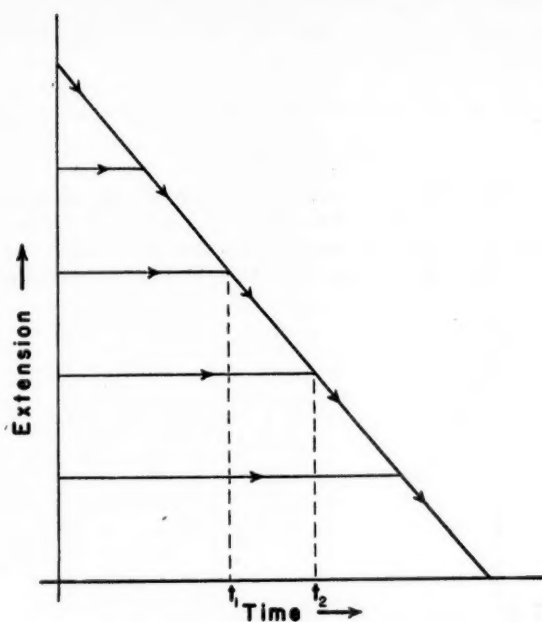


FIG. 24.

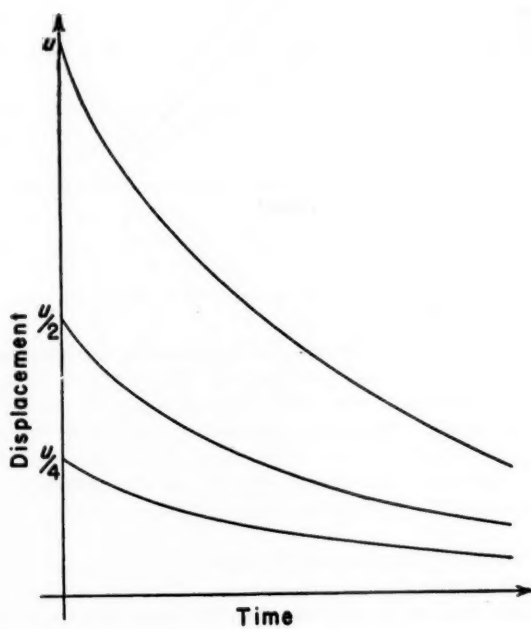


FIG. 25.

unstretched rubber at the free end of the sample. Since it is not the actual lengths but the displacements which are measured experimentally, we have chosen this type of curve to present our data.

Going back to Equation (1), let us consider the case involving large internal friction. Here the inertial term can be neglected and the solution becomes:

$$u(x, t) \cong \epsilon x e^{-(E/I)t} \quad (4)$$

In this case we neglect the wave pulse, and hence this equation holds only after the wave pulse has passed down the sample. A schematic drawing of this case is seen in Figure 25. Here we see that at any given time the displacement (and also the velocity) of any point on the sample is proportional to its dis-

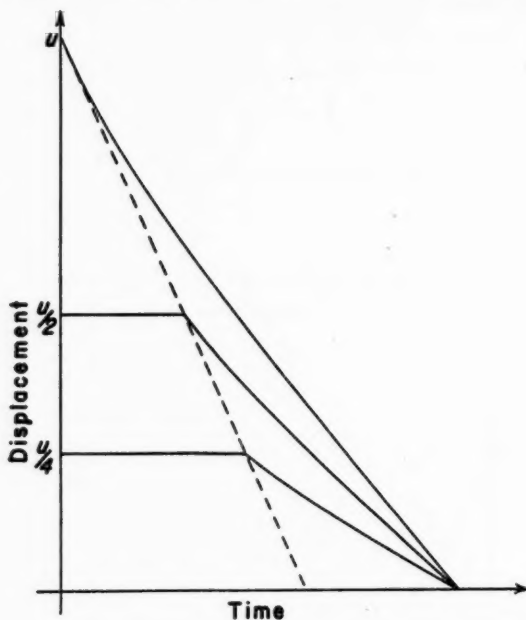


FIG. 26.

tance from the fixed end. Also, of course, the sample approaches the unstretched state exponentially with time.

The intermediate case may be treated by the Fourier method. However, since most experiments are not extremes, it is of interest to treat this case graphically. Figure 26 shows the wave pulse arriving at the fixed end before the sample has completely retracted. Of course, a point on the sample cannot move until the wave pulse arrives there, but after that its velocity depends somewhat on its position. The lower portions of the curves of Figure 26 are not accurate because of the fact that buckling sets in as soon as the wave pulse is reflected.

In the above considerations we have neglected the weight of the stylus and unstretched rubber at the tip (in the clamp). The effect of this would be to round off any sharp corners in Figures 22 to 26, especially the beginning of the curves. This accounts for the S-shape of some of the curves.

In our high-speed photos, Figures 19-21 (Hevea tread to Butyl tread), the reflection of the wave pulse at the fixed end will start the buckling.

So far our considerations have been of a very general nature, and will hold for rubberlike materials, as well as for steel. To find the difference between rubber and steel we have to correlate quantitatively the propagation of stress waves with the elastic constants of these materials. Obviously, the big factor ( $10^4$  dynes per sq. cm.) between Young's modulus for steel ( $E = 2 \times 10^{11}$ ) and rubber ( $E = 2 \times 10^7$ ) will cause quite a quantitative difference in the velocity of stress propagation.

First, we define precisely the velocity of stress propagation. Referring to Figure 23, we see that the velocity of the tip  $v_t$  is related to the velocity of the wave pulse  $v_p$  by the simple relation:

$$\frac{v_p}{v_t} = \frac{L}{L-1} = \frac{\epsilon+1}{\epsilon}; \quad \epsilon = L-1: \quad \text{Extension} \quad (5)$$

where  $L$  is the relative length;  $L = l/l_0$ ;  $l$  being the extended length and  $l_0$  the original length. The pulse travels from the stretched end down to the fixed end, while the tip moves only from the stretched end to the end in the unstretched state.

Next, we write the theoretical expression for  $v_p$  as obtained in the theory of James and Guth:

$$v_p = L(E/\rho)^{\frac{1}{2}} = (\epsilon+1)(E/\rho)^{\frac{1}{2}} \quad (6)$$

where  $E$  is Young's modulus, and  $\rho$  is the density.

For the velocity of the tip, Equations (1) and (2) yield:

$$v_t = (L-1)(E/\rho)^{\frac{1}{2}} = \epsilon(E/\rho)^{\frac{1}{2}} \quad (7)$$

We see that  $v_t$  goes to zero with the extension  $\epsilon$ , whereas  $v_p$  approaches the value  $(E/\rho)^{\frac{1}{2}}$ .

The validity of Hooke's law is assumed in deriving Equation (6). In addition internal friction was neglected. Therefore it should hold for the initial slope of the velocity vs. elongation curves for stocks like Hevea gum, where internal friction is comparatively small. The values of  $E$  and  $\rho$  were determined in this laboratory for the stock in question.

The duration of the retraction follows from Equation (6). Since the pulse travels the distance  $l$  with the uniform velocity  $v_p$ :

$$\tau = l/v_p = l_0/(E/\rho)^{\frac{1}{2}} \quad (8)$$

For  $l_0 = 10$  cm. and the above values of  $E$  and  $\rho$  we obtain:

$$t = 10 \text{ milliseconds}$$

$$v_p = 3.7 \times 10^3(\epsilon+1)$$

$$v_t = 3.7 \times 10^3(\epsilon)$$

The corresponding values for steel are:

$$t = 0.1 \text{ millisecond}$$

$$v_p = 1.6 \times 10^5(\epsilon+1)$$

$$v_t = 1.6 \times 10^5(\epsilon)$$

This comparison shows that the snapback of steel takes place on a time-scale one hundred times smaller than that for rubberlike materials.

For the differential extension (cf. Figure 22) this simple theory gives the result indicated in Figure 27, corresponding to instants indicated by dotted lines in Figure 24.

It was pointed out by James and Guth<sup>4</sup> that deviations from Hooke's law cause broadening of the contraction pulse. Consideration of momentum and energy transfer makes it evident at once that an acceleration pulse of fixed form and limited extent cannot occur except for a Hooke's law bar. Nevertheless, it is instructive to assume approximately the existence of an acceleration pulse of fixed form and limited extent, to apply the energy law, and to neglect its contradiction to the momentum theorem. According to the theory of James and Guth, all sections of the freely retracting sample move with the

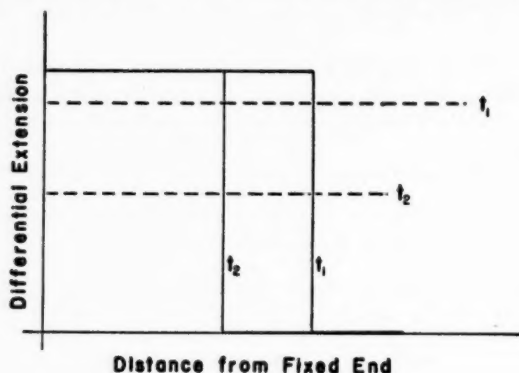


FIG. 27.

same constant velocity as the tip. The Expression (7) for  $v_t$  may be written in the form:

$$\sigma_0 \cdot \frac{1}{2} M v_t^2 = \int_{l_0}^l Z \sigma_0 dl \quad (9)$$

$$M = l_0 \sigma_0 \rho = \text{mass of the sample}$$

with:

$$Z = E \cdot \epsilon \quad (9a)$$

For the special problem of computing the velocity of the tip one may consider, therefore, the whole mass  $M$  of the sample as "effective". Equation (9) represents the energy theorem for a free vibration. An obvious generalization of Equation (9) is to replace  $Z$  by the theoretical stress-strain curve of the theory of James and Guth, instead of its Hookean approximation as in Equation (9a). Then one obtains the following equation with  $M/M^* = 1$ .

$$v = \left[ \frac{E}{3\rho} \times \frac{M}{M^*} \right]^{\frac{1}{2}} \left[ L^2 + \frac{2}{L} - 3 \right]^{\frac{1}{2}} \quad (10)$$

The actual experiments show that all sections of the freely retracting sample do not move with exactly the same velocity. A  $v(x)$  vs.  $v(l) = v_t$  curve may be derived from our two stylus experiments.  $v(x)$  denotes here the velocity at any point at a distance  $x$  from the fixed end of the sample. From this curve the kinetic energy may be computed by the approximate Rayleigh method.

Equating the result to  $\frac{1}{2}Mv_r^2$  one obtains  $M/M^*$ . It depends somewhat on the particular elongation. A determination gave  $M/M^*$  equal to 0.85. This value is used in Figure 28 for computing the curve labelled "theory". The agreement is rather good for low extensions, as would be expected.

Using  $M/M^* = 3$  is equivalent to assuming the relation:

$$v(x) = \frac{x}{l} v(l) \quad (11)$$

Equation (11) does not hold at all according to our experiments with Hevea and GR-S. For Butyl tread, however, Equation (11) is a rough approximation. The dotted lines in Figure 27 refer to Equation (11) and should be compared

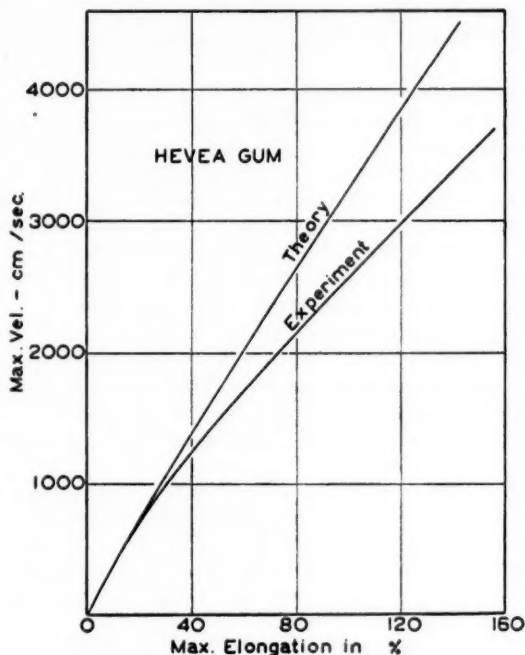


FIG. 28.

with the dotted lines in Figure 22. It should be stressed that a horizontal line in a plot of the differential extension *vs.* distance from the fixed end can mean, either that the sections of the same do not move at all, or that they move according to Equation (11).

The correct explanation of the behavior of Butyl tread rests, of course, on the Equation (1) or to a fair approximation, on the solution (4).

In general the introduction of a concentrated mass, *i.e.*, the passing from an elastic solid to a point mass, is justified only if during a period the wave pulse traverses the sample several times.

The correct treatment of the anharmonic case rests, of course, on the wave equation:

$$\rho \frac{\partial^2 u}{\partial t^2} = \frac{dZ}{dL} \cdot \frac{\partial^2 u}{\partial x^2} \quad (12)$$

Here  $L = \partial u / \partial x$ , and  $dZ/dL = dZ/d\epsilon$ , the differential Young's modulus because of the linear connection between  $L$  and  $\epsilon$ . For  $Z = Z(L)$  we may substitute the experimentally obtained stress-strain curve of a particular stock, or the theoretical equation by James and Guth.

$$Z = K(L - 1/L^2) \quad (13)$$

where  $K$  is 3 times Young's modulus best taken from experiment (slope of the stress-strain curve at small extensions).

From (12) one obtains:

$$v_t = \left( \frac{1}{\rho} \cdot \frac{dZ}{dL} \right)^{1/2} \quad (14)$$

This expression checks with experiment much better than Equation (10), and yields a  $v_t$  vs.  $\epsilon$  curve of similar shape to the corresponding stress-strain curve.

In 1874 Exner, using an ingenious method devised by Stefan<sup>5</sup>, measured the time ( $\tau$ ) needed by the wave pulse to arrive from the free to the fixed end. His value for unstretched rubber  $v_p = 3740$  cm. per second is in fair agreement with the value obtained by us for another compound by extrapolation ( $v_p = 3800$  cm. per second). The method of Exner-Stefan is sound in principle. However, the interpretation of  $v_p$  for stretched rubber is left open by his work. Exner's aim was to obtain the dependence of  $E$  on temperature. For the case of stretched rubber, however, relaxation effects mask the true dependence. This fact was not known at that time. It is not clear why Exner did not obtain the correct dependence for the unstretched state. Recent work at Notre Dame University and at the Bureau of Standards shows conclusively that  $E$  increases with rising temperature. This was checked in our work for both extension and compression.

Irons<sup>6</sup> obtained  $v_p = 15,600$  cm. per second for ebonite, using another method also developed by Stefan.

The velocity of a wave pulse, i.e., the velocity of a sound in a rodlike sample, is about 50 times smaller than the usually so-called "velocity of sound" in an infinite medium. In a rod, extension is accompanied by lateral contraction, which is not true for an infinite medium. Only for a substance with a very small Poisson's constant (a substance like cork) will the two velocities be comparable.

#### REFERENCES

- <sup>1</sup> Mrowca, Dart and Guth, *Phys. Rev.* **66**, 30 (1944); see also Stambaugh, *Phys. Rev.* **65**, 250 (1944). A comparison of the Goodyear and Notre Dame work will be given in a later issue of this journal.
- <sup>2</sup> This stock had the same composition as that used by Roth and Wood (*J. Applied Physics* **15**, 749 (1944)).
- <sup>3</sup> Mrowca, Dart and Guth, *Phys. Rev.* **66**, 32 (1944).
- <sup>4</sup> James and Guth, *Phys. Rev.* **66**, 33 (1944).
- <sup>5</sup> Quoted by Whitby, "Plantation Rubber and the Testing of Rubber," Longmans and Green, London, 1920, p. 461.
- <sup>6</sup> Irons, *J. Sci. Instruments* **7**, 323 (1930).

# THE THERMODYNAMICS OF RUBBER AT SMALL EXTENSIONS \*

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## DISCUSSION OF MEYER AND FERRI'S CONCLUSIONS

On the assumption of reversible stretching, Wiegand and Snyder<sup>1</sup> derived the following thermodynamic relationship:

$$\left(\frac{\partial E}{\partial L}\right)_{T,P=0} = F - T \left(\frac{\partial F}{\partial T}\right)_{L,P=0} \quad (1)$$

where  $F$  is the force keeping the elastomer in a stretched condition. Meyer and Ferri<sup>2</sup> concluded from an equivalent equation that, if  $(\partial E/\partial L)_{T,P=0} = 0$ , then  $F$  measured at constant extension should vary directly as the absolute temperature. Mathematically:

$$F = GT; \quad P = 0, \quad L = \text{constant} \quad (2)$$

where  $G$  is the constant of proportionality. Experimentally, Meyer and Ferri found a linear relationship between the temperature and force, but not proportionality. They were led to the assumption that, since the length of the unstretched rubber changes as a result of thermal expansion, the force requires a temperature correction. For example, the corrected force is:

$$F_c = F + M\beta(T - T_0) \quad (3)$$

where

$$\beta = \frac{1}{L} \left(\frac{\partial L}{\partial T}\right)_{D,P=0}$$

and

$$M = L \left(\frac{\partial F}{\partial L}\right)_{T,P=0}$$

$D$  is the deformation or the ratio of two perpendicular lengths, one normal to the direction of stress and one parallel to it. They found that this corrected force was proportional to the absolute temperature:

$$F_c = aT \quad (4)$$

when  $P$  and  $L$  are constants; and it was concluded that  $(\partial E/\partial L)_{T,P=0} = 0$ .

Equation (1) does not assume that the length of an unstretched rubber sample remains constant during temperature variations. The equation of state from which this equation is derived contains the assumption that the force is a function of the temperature, and therefore, no corrections to include this fact are necessary. Therefore, the conclusion drawn from Equation (4) is in error;  $(\partial E/\partial L)_{T,P=0} \neq 0$ .

\* Reprinted from the *Journal of Applied Physics*, Vol. 16, No. 1, pages 50-54, January 1945. This paper was presented before the Inaugural Meeting of the Division of High Polymer Physics of the American Physical Society, Rochester, N. Y., June 24, 1944.

## THE CHANGE IN INTERNAL ENERGY WITH EXTENSION

To examine the implications of Meyer and Ferri's data, another variable, the hydrostatic pressure ( $P$ ), must be considered. This variable is introduced so that the volume of the sample may be made independent of the extension and temperature. The entire testing environment, weights, sample, and all will be considered immersed in a non-buoyant fluid that does not penetrate the rubber and whose pressure is variable at will (see Figure 1).

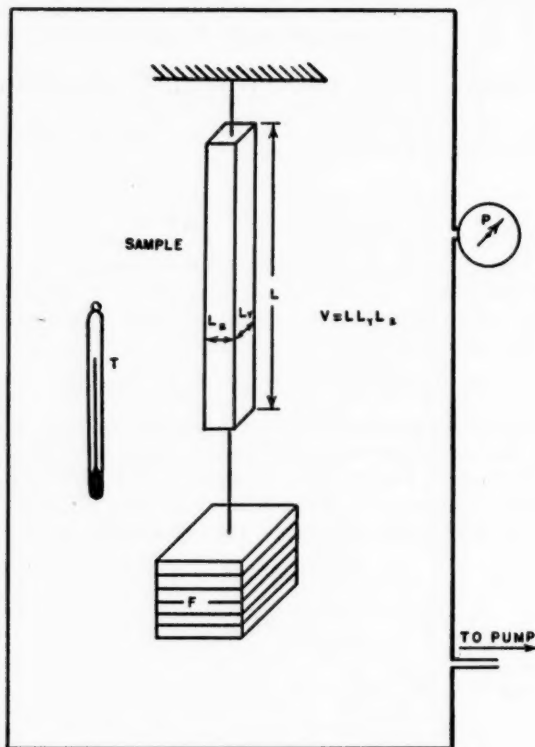


FIG. 1.—Schematic diagram of extended sample in its testing environment.

Below the range of extensions in which crystallization takes place, the stretching of rubber is a reversible phenomenon, if sufficient time is allowed for the sample to come to equilibrium. Thus at equilibrium and for small extensions the properties of the rubber are determined by its temperature, length, and the hydrostatic pressure of the fluid in which it is immersed; *e.g.*:

$$E = E(T, P, L) \quad (5)$$

$$S = S(T, P, L) \quad (6)$$

$$V = V(T, P, L) \quad (7)$$

where  $S$  is the entropy, and  $V$  is the volume. From the first law of thermodynamics:

$$T\delta S - \delta E - P\delta V + F\delta L = 0 \quad (8)$$

Therefore, from Equations (5) to (8):

$$F = F(T, P, L) \quad (9)$$

Expanding Equations (5) to (7); and substituting in Equation (8), we obtain:

$$\begin{aligned} T[(\partial S/\partial T)\delta T + (\partial S/\partial P)\delta P + (\partial S/\partial L)\delta L] - [(\partial E/\partial T)\delta T \\ + (\partial E/\partial P)\delta P + (\partial E/\partial L)\delta L] - P[(\partial V/\partial T)\delta T \\ + (\partial V/\partial P)\delta P + (\partial V/\partial L)\delta L] + F\delta L = 0 \quad (10) \end{aligned}$$

Since  $T$ ,  $P$ , and  $L$  are independent variables;  $\delta T$ ,  $\delta P$ , and  $\delta L$  may be chosen independently of each other. Thus from Equation (10):

if  $\delta P = \delta L = 0$ :

$$T(\partial S/\partial T) - (\partial E/\partial T) - P(\partial V/\partial T) = 0, \quad \text{when} \quad \delta T \neq 0$$

if  $\delta T = \delta L = 0$ :

$$T(\partial S/\partial P) - (\partial E/\partial P) - P(\partial V/\partial P) = 0, \quad \text{when} \quad \delta P \neq 0$$

if  $\delta P = \delta T = 0$ :

$$T(\partial S/\partial L) - (\partial E/\partial L) - P(\partial V/\partial L) + F = 0, \quad \text{when} \quad \delta L \neq 0 \quad (11)$$

Solving for the entropy terms in Equation (11) we get:

$$\partial S/\partial T = 1/T[(\partial E/\partial T) + P(\partial V/\partial T)]$$

$$\partial S/\partial P = 1/T[(\partial E/\partial P) + P(\partial V/\partial P)]$$

and

$$\partial S/\partial L = 1/T[(\partial E/\partial L) + P(\partial V/\partial L) - F] \quad (12)$$

Since by mathematical identity:

$$\partial^2 S/\partial P \partial T = \partial^2 S/\partial T \partial P$$

$$\partial^2 S/\partial T \partial L = \partial^2 S/\partial L \partial T$$

$$\partial^2 S/\partial L \partial P = \partial^2 S/\partial P \partial L$$

it follows from Equation (12) that:

$$(\partial E/\partial P)_{T,L} = -P(\partial V/\partial P)_{T,L} - T(\partial V/\partial T)_{P,L} \quad (13)$$

$$(\partial E/\partial L)_{T,P} = F - T(\partial F/\partial T)_{P,L} - P(\partial V/\partial L)_{T,P=0} \quad (14)$$

and

$$(\partial V/\partial L)_{T,P} = (\partial F/\partial P)_{L,T} \quad (15)$$

For zero hydrostatic pressure Equation (14) reduces to the Wiegand and Snyder equation.

It follows from Equations (5) and (7) that  $E = E(T, P(V, L, T), L)$ . By differentiating  $E$  partially with respect to length, we get:

$$(\partial E/\partial L)_{V,T} = (\partial E/\partial L)_{P,T} + (\partial E/\partial P)_{T,L}(\partial P/\partial L)_{V,T} \quad (16)$$

Similarly from Equations (7) and (9):

$$(\partial P/\partial V)_{F,T} = (\partial P/\partial V)_{L,T} + (\partial P/\partial L)_{V,T}(\partial L/\partial V)_{F,T} \quad (17)$$

Equation (16) is an alternative expression of the term  $(\partial E/\partial L)_{V,T}$  for which we

are solving. The relation does not consist as yet of experimentally observed quantities. The two partial derivatives of the internal energy, however, are already expressed in familiar experimental terms in Equations (13) and (14). Now, we must find such an expression for the partial derivative of the pressure with respect to length.

From Equations (7) and (9),  $P = P(V, L, T)$ . Thus by identity:

$$(\partial P/\partial L)_{V,T} = -(\partial P/\partial V)_{L,T}(\partial V/\partial L)_{P,T} \quad (18)$$

and, therefore:

$$(\partial P/\partial V)_{F,T} = (\partial P/\partial V)_{L,T}[1 - (\partial V/\partial L)_{P,T}(\partial L/\partial V)_{F,T}] \quad (19)$$

Expanding the right-hand side of Equation (15), we get:

$$(\partial V/\partial L)_{P,T} = -(\partial F/\partial L)_{P,T}(\partial L/\partial P)_{F,T} \quad (20)$$

Substituting Equations (19) and (20) in (18) we are able to evaluate  $(\partial P/\partial L)_{V,T}$ :

$$(\partial P/\partial L)_{V,T} = (\partial P/\partial V)_{F,T}(\partial F/\partial L)_{P,T}(\partial L/\partial P)_{F,T} / \left[ 1 + \left( \frac{\partial F}{\partial L} \right)_{P,T} \left( \frac{\partial L}{\partial P} \right)_{F,T} \left( \frac{\partial L}{\partial V} \right)_{F,T} \right] \quad (21)$$

The partial derivatives in Equation (21) can be replaced in general by more common moduli, *e.g.*:

$$\begin{aligned} M &= L(\partial F/\partial L)_{P,T} \\ Y &= ML/V \\ K &= -V(\partial P/\partial V)_{F,T} \\ \beta_1 &= (\frac{1}{3}V)(\partial V/\partial T)_{L,P=0} \\ A &= (3V/L)(\partial P/\partial V)_{F,T}(\partial L/\partial P)_{F,T} = (3V/L)(\partial L/\partial V)_{F,T} \end{aligned} \quad (22)$$

$M$  is the stress-strain modulus,  $Y$  is Young's modulus,  $K$  is a bulk modulus, and  $\beta_1$  is a thermal coefficient of linear expansion.  $A$  is the anisotropy factor which is described in detail in a later section. It is sufficient to mention here that  $A = 1$  for isotropic rubber.

When  $YA/k$  is small compared to 9,  $\beta_1$  is very nearly equal to the coefficient of expansion measured at constant deformation and zero hydrostatic pressure. This may be proven in the following manner.

Since  $D = D(T, P, L)$ , it can be shown, in a manner similar to the derivation of Equation (12), that:

$$(\partial V/\partial T)_{D,P} = (\partial V/\partial T)_{L,P} + (\partial V/\partial L)_{P,T}(\partial L/\partial T)_{D,P} \quad (23)$$

In addition by identity:

$$(\partial F/\partial P)_{L,T} = -(\partial F/\partial L)_{P,T}(\partial L/\partial P)_{F,T} \quad (24)$$

and

$$(\partial L/\partial P)_{F,T} = (\partial L/\partial V)_{F,T}(\partial V/\partial P)_{F,T} \quad (25)$$

Substituting Equations (15), (24), (25) in Equation (23) we obtain the following expression:

$$(\partial V/\partial T)_{D,P} = (\partial V/\partial T)_{L,P} - (\partial L/\partial V)_{F,T} \times (\partial F/\partial L)_{P,T}(\partial L/\partial T)_{D,P}(\partial V/\partial P)_{F,T} \quad (26)$$

In terms of the coefficients and moduli already used, Equation (26) becomes:

$$3V\beta = 3V\beta_1 + \left(\frac{AL}{3V}\right)\left(\frac{V}{K}\right)\left(\frac{VY}{L^2}\right)(BL) \quad (27)$$

or

$$\beta = \beta_1/(1 - AY/9k) \quad (28)$$

If  $YA/k \ll 9$ ,  $\beta \doteq \beta_1$ . Substituting relations (22) into Equation (21), we obtain:

$$(\partial P/\partial L)_{V,T} = (MA/3V)/(1 - YA^2/9k) \quad (29)$$

or

$$(\partial P/\partial L)_{V,T} \doteq (MA/3V), \quad \text{when} \quad YA^2/k \ll 9 \quad (30)$$

Substituting Equations (13), (14), (22), and (30) in Equation (16) we obtain the equation:

$$(\partial E/\partial L)_{V,T} = F - T(\partial F/\partial T)_{P,L} - M\beta TA \quad (31)$$

#### ANISOTROPY FACTOR, $A$

The term  $A$ , defined in Equations (22), is measured only with difficulty. Nevertheless, its value for an isotropic elastomer can be predicted. This quantity will be referred to as the anisotropy factor. The significance of  $A$  becomes evident, if the effect of a change in hydrostatic pressure on the dimensions of a rectangular rubber strip is examined. Maintaining the force and temperature constant, the three perpendicular dimensions taken along the principal axis of the strain tensor will vary in the following manner:

$$\delta L = L\alpha_L\delta P, \quad \delta L_Y = L_Y\alpha_Y\delta P, \quad \delta L_Z = L_Z\alpha_Z\delta P \quad (32)$$

where the  $\alpha$ 's are coefficients of extensibility. That is to say, the change in a dimension in the direction of an axis of the strain tensor is proportional to its length and to the change in pressure. The corresponding change in volume is:

$$\delta V = LL_YL_Z - (L + \delta L)(L_Y + \delta L_Y)(L_Z + \delta L_Z) \quad (33)$$

It follows from Equations (32) and (33) that if  $\delta P \rightarrow 0$ :

$$\frac{3V}{L} \left( \frac{\partial L}{\partial V} \right)_{F,T} = \frac{3\alpha_L}{\alpha_L + \alpha_Y + \alpha_Z} \quad (34)$$

and from Equations (22) and (34):

$$A = 3\alpha_L/(\alpha_L + \alpha_Y + \alpha_Z)$$

Where the material is isotropic, the  $\alpha$ 's are all equal and  $A$  is 1. This condition is met for ordinary rubber at zero extension, and is met approximately at small extensions. For anisotropic conditions the extensibilities in the directions normal to the direction of stress may or may not equal the extensibility in the stress direction. Thus, as the material becomes anisotropic,  $A$  may differ from 1. At small extensions when  $A \doteq 1$ , Equation (31) becomes:

$$(\partial E/\partial L)_{V,T} = F - T(\partial F/\partial T)_{L,P=0} - M\beta T \quad (35)$$

#### ANALYSIS OF MEYER AND FERRI'S DATA

From Equations (3) and (4), which summarize the Meyer and Ferri data, for small extensions:

$$F = aT - M\beta(T - T_0) \quad (36)$$

Differentiating partially with respect to temperature, we obtain:

$$(\partial F/\partial T)_{L,P=0} = a - M\beta - \beta(T - T_0)(\partial M/\partial T) \quad (37)$$

Substituting the values of  $F$  and its partial derivative as given by Equations (36) and (37) into Equation (35), the following relation results:

$$(\partial E/\partial L)_{V,T} = M\beta T_0 + \beta T[(T - T_0)(\partial M/\partial T) - M]$$

and letting  $T \rightarrow T_0$ :

$$(\partial E/\partial L)_{V,T} = 0 \quad (38)$$

Similarly from Equations (36), (37) and (1):

$$(\partial E/\partial L)_{T,P} = M\beta T, \quad P = 0 \quad (39)$$

Thus, we see from Equations (38) and (39) that the Meyer and Ferri data require that:

$$(\partial E/\partial L)_{V,T} = 0$$

and not that  $(\partial E/\partial L)_{P,T} = 0$ .

#### STRUCTURAL CHANGES IN RUBBER DURING EXTENSION

Relations (38) and (39) are indicative of the major processes that take place in rubber on extension. There are three possible mechanisms for the isothermal absorption of the extension energy in an elastomer. One is the distortion of the valence angles, the second is the separation of adjacent atoms, and a third is the orientation of the molecules.

In rubber the valence angle distortion mechanism is not consistent with the data of Meyer and Ferri. The energy absorbed in distorting the valence angles would appear as an increase in the internal energy. It should be noted that a change in valence angles is not necessarily accompanied by a change in volume, since all volume changes that would normally occur on extending rubber can be eliminated by varying the hydrostatic pressure. Thus, a change in valence angle would result in an increase of the internal energy of the rubber even for isothermal stretching at constant volume. This is in direct contradiction to Equation (38) which states that there is no internal energy change if the volume and temperature are constant.

According to Equations (38) and (39), on isothermal extension, the internal energy of rubber increases only when the volume is allowed to grow. Since an increase in volume necessarily means that the average interatomic distance becomes greater, the internal energy stored in the rubber on isothermal stretching must be taken up in pulling the atoms apart.

The change in the average interatomic distances cannot, however, be the sole means by which energy is absorbed on stretching. This is particularly obvious in the case of rubber extended isothermally at constant volume, for there is no internal energy accumulation under these conditions, and yet work is done on the rubber. According to the first law of thermodynamics:

$$-\delta W = \delta E - T\delta S, \quad T\delta S = \delta Q \quad (40)$$

where  $S$  is the entropy and  $W$  is the work performed by the sample on its surroundings. The quantity  $T\delta S$  is the increase of isothermally unavailable energy. In a system undergoing thermal agitation,  $S$  is a measure of the amount of molecular or atomic disorder. Therefore,  $-T\delta S$  might be referred to as the change in orientation energy. Equation (40) indicates that the work

of extension divides itself between the internal energy and the orientation energy. Since the change in orientation energy is equal to the heat given up by the rubber, the portion of the work that causes the orientation appears as heat, having made an equal amount of the rubber's internal energy isothermally available.

Based on the conclusion that the internal energy change is entirely owing to interatomic displacements, either Equation (9) or (39) permits the calculation, from experimental data, of how the energy taken up in stretching the rubber is divided between the orientation energy and interatomic displacement energy. Thus, since the differential work input on stretching is:

$$-\delta W = F\delta L \quad (41)$$

and from Equation (39):

$$\delta E = (\partial E / \partial L)_{T, P=0} \delta L = M\beta T \delta L \quad (42)$$

therefore, from Equations (41) and (42):

$$(\delta E / \delta W) \times 100 = 100M\beta T / F \text{ per cent} \quad (43)$$

Where  $(\partial E / \partial L) = 0$ , Equations (9) and (39) yield the following relationship:

$$(\delta E / \delta W) \times 100 = [(1 - T/F)(\partial F / \partial T)_{L, P=0}] \times [100] \text{ per cent} \quad (44)$$

In Equation (43) the ratio is calculated from stress-strain data, while Equation (44) requires thermal data. It should be noted that both relations hold only when  $(\partial E / \partial L)_{V, T} = 0$ , but that Equation (43) has the additional requirement that  $A$  is approximately 1. Meyer and Ferri's data indicate that the interatomic displacement absorbs the entire energy input at 8 per cent extension. For, at this extension  $(\partial F / \partial T)_{L, P=0} = 0$  and Equation (44) reduces to  $\delta E / \delta W = 1$ . The terms  $M$  and  $\beta$  do not vary much with the strain of the rubber, although they do decrease somewhat. Thus above 8 per cent extension and in the range for which Equation (43) is true, the relative contribution of the interatomic displacement energy to the total retractive energy decreases with increasing force.

#### EQUATION OF STATE

The form of the equation of state of rubber at low extensions also follows from the data of Meyer and Ferri. If in Equations (5)–(8)  $V$ ,  $L$ , and  $T$  are used as independent variables instead of  $P$ ,  $L$ , and  $T$ ; the equation that corresponds to Equation (31) is:

$$(\partial E / \partial L)_{V, T} = F - T(\partial F / \partial T)_{V, L} \quad (44)$$

Now, according to Equation (38),  $(\partial E / \partial L)_{V, T} = 0$  and Equation (44) becomes:

$$F = T(\partial F / \partial T)_{V, L} \quad (45)$$

Therefore:

$$F = T\psi(V, L) \quad (46)$$

where  $\psi$  is an undetermined function of  $V$  and  $L$  that must be consistent with Equation (15). The final relation, Equation (46), gives the form of the equation of state of rubber at low extensions as required by the data of Meyer and Ferri.

## SUMMARY

On analyzing their own data, Meyer and Ferri have concluded that, at small extensions, rubber is an ideal elastomer according to the definition that  $(\partial E/\partial L)_{P,T} = 0$ . Further analysis of Meyer and Ferri's data does not sustain their conclusion. If, however,  $(\partial E/\partial L)_{V,T} = 0$  is taken as a new criterion for an ideal elastomer, Meyer and Ferri's data do indicate that rubber is ideal, at least for extensions up to 166 per cent. The new criterion implies that the valence angles do not store an appreciable amount of energy when the rubber is stretched. However, both the molecular orientation and the interatomic displacements do influence the energy required for extension.

## TABLE OF SYMBOLS

- A Anisotropy factor,  $\frac{3V}{L} \left( \frac{\partial L}{\partial V} \right)_{P,T}$ .
- D Deformation, the ratio of two perpendicular dimensions, one taken in the direction of stress, and one normal to this direction.
- E Total internal energy, or intrinsic energy.
- F Force acting on a rubber sample keeping it in a stretched condition.
- F<sub>c</sub> Corrected force of Equation (3).
- G Proportionality constant of Equation (2).
- K Compression modulus at constant load and temperature,  $-V(\partial P/\partial V)_{F,T}$ .
- L Length of the sample in the direction of stress.
- L<sub>v</sub> Dimension of rectangular sample normal to the direction of stress.
- L<sub>z</sub> Dimension of rectangular sample perpendicular to both L and L<sub>v</sub>.
- M Extension modulus of the sample,  $L(\partial F/\partial L)_{P,T}$ .
- P Hydrostatic pressure of the medium in which the test is performed.
- Q Heat absorbed by the sample from its surrounding.
- S Entropy.
- T Absolute temperature.
- V Volume of the sample.
- W Work performed by the rubber sample on its surroundings.
- Y Young's modulus,  $\frac{L^2}{V} \left( \frac{\partial F}{\partial L} \right)_{P,T}$ .
- $\alpha$  Coefficient of extensibility,  $\frac{1}{L} \left( \frac{\partial L}{\partial P} \right)_{F,T}$ .
- $\beta$  Thermal coefficient of linear expansion at constant deformation and at zero pressure,  $\frac{1}{L} \left( \frac{\partial L}{\partial T} \right)_{D,P=0}$ .
- $\beta_1$   $\frac{1}{3}$ rd thermal coefficient of volume expansion at constant length and at zero pressure,  $\frac{1}{3V} \left( \frac{\partial V}{\partial T} \right)_{L,P=0}$ .

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## SOME PHYSICAL PROPERTIES OF ELASTOMERS AT LOW TEMPERATURE \*

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### INTRODUCTION

The design of a laboratory test to duplicate the service performance of a product is always difficult. When carried out carefully, it becomes as involved as a direct use test. To circumvent these difficulties in low temperature measurements, we have chosen to measure well defined constants over a range of independent variables. From an interpretation of these data, one can predict performance in a way not possible by service-simulating tests. The analysis does, however, demand an understanding of the physical nature of stress-strain properties, including at least a qualitative understanding of the mechanism involved.

Below the second-order transition temperature<sup>1</sup> an elastomer is hard and brittle. This glassy state is characterized by an elastic modulus in the neighborhood of  $10^7$  lbs. per sq. in.<sup>2</sup> As the temperature increases, the modulus decreases rapidly along a sigmoidal curve until the modulus has reached a value of approximately  $10^2$  lbs. per sq. in. With further increase in temperature the modulus increases linearly with absolute temperature in a manner successfully explained by the kinetic thermodynamic approach<sup>3</sup>. The modulus-temperature curve consists, then, of three parts: (1) a glassy region; (2) a transition; (3) an elastic region.

The value of the stress for a given strain at any temperature depends on the ratio of the test interval to the time required for equilibrium to be established. The ratio decreases as the temperature decreases until, in the transition region, equilibrium is not established in an interval at all comparable with the testing time. Here, the values of the modulus, or any other elastic property, depend greatly on the testing rate, as shown in Figure 1. To obtain these data the samples were stressed at the temperature of testing and the strain was measured at different times.

For short time tests the transition curve is less abrupt, and stiffening begins at relatively high temperatures. For long-time tests the modulus decreases with decreasing temperature, as predicted by thermodynamic theories. The infinite time curve of Figure 1 was taken at true thermodynamic equilibrium by measuring the stress required to hold the sample at fixed length as the temperature is decreased slowly—a so-called isometric<sup>4</sup>. No correction was made for the thermal expansion of the supporting structure. The physical mechanism associated with the transition region has never been described completely, but it is clear that the phenomenon is associated with a change in molecular relaxation times<sup>5</sup>.

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In many uses a rubberlike material with a modulus greater than five times its value at room temperature is unsuitable. In these cases the temperature at which the material becomes glassy is not useful for evaluation. Measurements of the physical properties as a function of temperature are required.

#### EXPERIMENTAL

Very little of the work in the literature<sup>6</sup> deals with such variations, and there is almost none that records values for moderate elongations (about 100 per cent) and low testing rate (around 100 lbs. per sq. in. per min.), determined on previously flexed samples measured in tension.

To supply the required data a simple test apparatus has been designed. In general the sample is extended by means of force applied to the free end through a cable extending out of the test-chamber to a measuring head. Either of two methods can be used for the determination of the stress and strain. One is for exploratory work in which a large number of samples are involved; the other is valuable when complete curves are required.

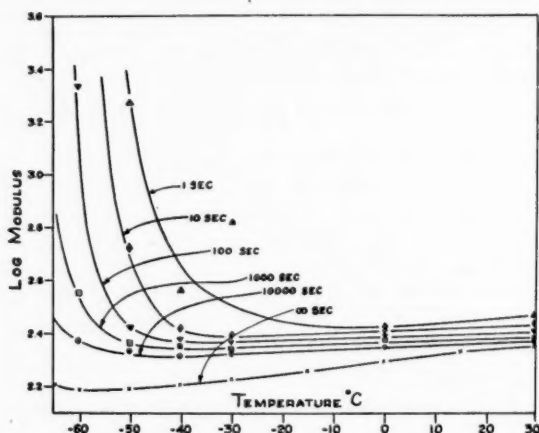


Fig. 1.—Time dependence of modulus vs. temperature curve for a pure-gum natural-rubber stock. Modulus calculated from strain after recorded times have elapsed.

The first device is indicated in Figure 2. To the free end of the sample is attached a cable which extends around a pulley, out of the refrigerator, and over another pulley to a weight pan. Attached to the external pulley and in front of a scale is a pointer which indicates the length of wire which passes, and hence, the sample elongation.

With this set-up the grips are attached and the sample is flexed to 100 per cent several times by hand at room temperature, and then placed in the refrigerator at  $-70^{\circ}\text{C}$ . When the conditioning time has elapsed, the sample is moved into position, and enough granulated lead is added, at a fixed rate of 1 lb. per min., to the pan to produce 100 lbs. per sq. in. stress above the tare weight. The resulting extension is read on the scale and the modulus is calculated. The experiment is repeated at  $10^{\circ}$  intervals up to  $30^{\circ}\text{C}$ , allowing approximately one-half hour conditioning time at each temperature<sup>7</sup>. The relaxed sample length used for calculating percentage strain is then measured.

In the second method the entire stress-strain curve is recorded by a simple device designed to measure both stress and strain on a single wire from the test chamber<sup>8</sup>.

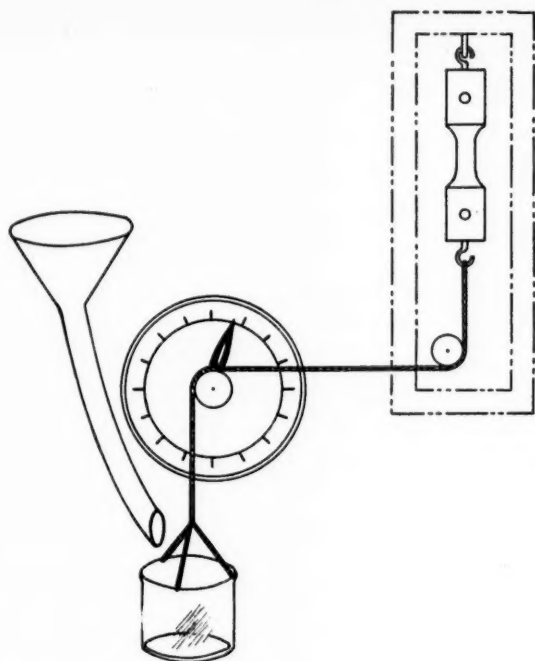


FIG. 2.—Diagram of the apparatus used for the single-point method of determining modulus.

When complete information on one stock is desired, this machine is used. The sample is placed in the refrigerator unflexed, and is given a definitely prescribed history. The most common procedure is to extend the samples at the testing rate to 100 lbs. per sq. in. and back to zero stress four times without pause before recording the stress-strain curve. Further cycles give almost reproducible curves (Figure 3). A different sample is used at each tempera-

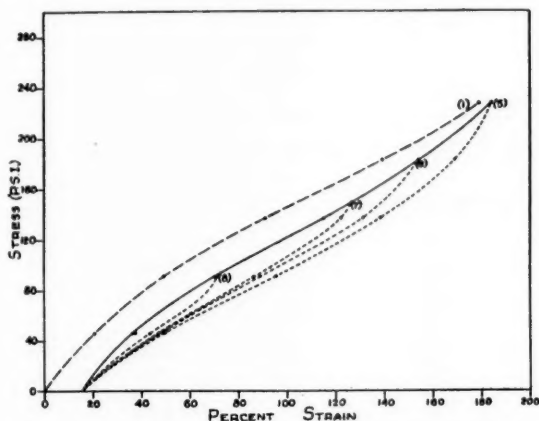


FIG. 3.—The complete stress-strain curve of the first, fifth, sixth, seventh, and eighth cycles. Pure-gum rubber stock at  $-42^{\circ}\text{C}$ .

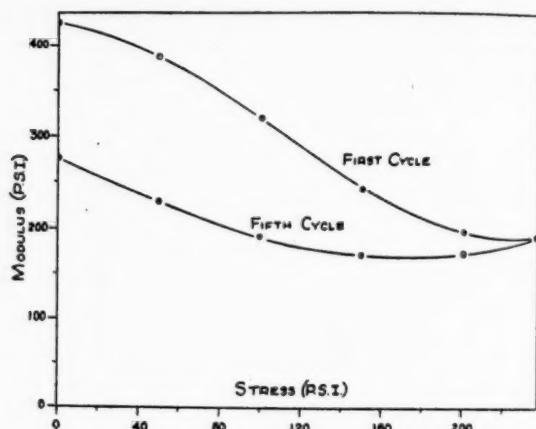


Fig. 4.—Modulus at different stresses for first and fifth cycles. A GR-S stock at 24° C.

ture when the modulus on the first cycle is also desired. The equilibrium cycle at a number of temperatures is shown in Figure 4.

#### EFFECT OF SOME INDEPENDENT VARIABLES

For the preliminary evaluation of stocks it is usually sufficient to determine the modulus at a single stress. The first method gives this value with sufficient accuracy, as is shown in Table I.

TABLE I  
COMPARISON OF TWO WAYS TO MEASURE MODULUS OF A RUBBER STOCK

Temperature ° C	Modulus (lbs. per sq. in.)	
	First method	Second method
31	177	162
0	165	165
-15	169	170
-31	174	175
-40	178	180
-50	257	252
-60	3570	3000

TABLE II  
ERROR IN STRAIN MEASURED BY SEPARATION OF GRIPS

Percentage separation of grips	Elongation between gauge marks divided by elongation between grips
0	1.00
10	0.985
20	0.975
30	0.968
40	0.962
50	0.956
60	0.952
80	0.944
100	0.937
140	0.932
180	0.931
200	0.930

In both methods the elongation is determined by measuring the separation between grips. The error introduced in the strain values is shown in Table II.

The flared ends of the sample necessary for satisfactory gripping account for this correctable error.

By recording the stress-strain curve through several cycles by the use of the single-wire stress-strain machine, most of the desired properties of the elastomers can be measured. Such a complete set at one temperature is shown in Figure 3. From these curves the modulus at any low stress for any cycle, the hysteresis, the set, and the effect of stress on modulus or hysteresis may be determined.

For a material which does not follow Hooke's law some care must be used in specifying the meaning attached to the modulus of elasticity. In this work the ratio of the stress to the strain calculated at a stress of 100 lbs. per sq. in. is used. In the recorded curves this is equivalent to the secant of the curve. The single-point technique gives the strain at 100 lbs. per sq. in., and hence, a similar measure of modulus. To conform with the customs of the rubber industry the strain is given as the ratio of the increase in length to the original length, and thus the modulus may be said to be the stress required to double the length if Hooke's law were obeyed.

The hysteresis is here defined as a percentage energy loss in a cycle; *i.e.*, the ratio of the area in the loop to the area under the ascending stress-strain curve. The set is recorded as the ratio of the remaining elongation to the initial elongation. It is not a permanent set, but applies to one testing speed only.

The absolute values of the properties defined depend very greatly on the testing technique. The effect of speed of testing was shown in Figure 1. The effect of shape of sample is shown in Table III.

TABLE III  
EFFECT OF WIDTH OF SAMPLE ON MODULUS

Pure-gum rubber—3 inches long—0.1 inch thick				
Temperature (° C)	Modulus (p.s.i.)			
	Width— $\frac{1}{4}$ inch	1 inch	2 inches	3 inches
30	80	118	134	146
0	79	120	129	139
-15	83	131	132	143
-30	93	177	142	155
-40	119	196	159	166
-50	247	277	190	302
-60	2360	2770	2820	2870

The effect of the previous history was shown in part in Figure 3, but is shown in a different way in Figure 4.

By proper attention to the factors considered above it is possible to learn much about low temperature properties of stocks. Figure 5 shows the fifth or equilibrium cycle for a stock at a number of temperatures.

## RESULTS

Figure 6 shows the temperature dependence of the modulus of elasticity in tension for a number of pure-gum stocks, determined by the single-point method. Relative modulus, used as the ordinate, is defined as the ratio of the modulus at any temperature to that at +30° C. It may be observed that a natural-rubber stock has approximately its designed modulus to within a few

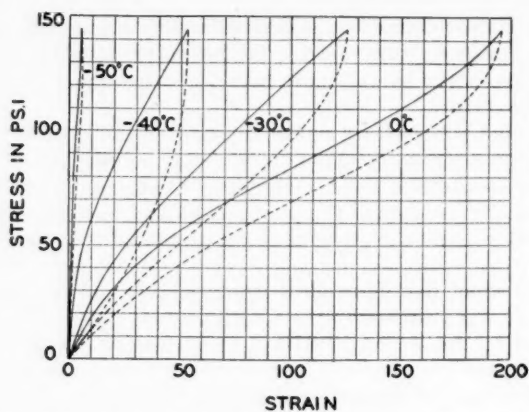


FIG. 5.—The fifth-cycle hysteresis loop at four temperatures. Neoprene-rubber stock.

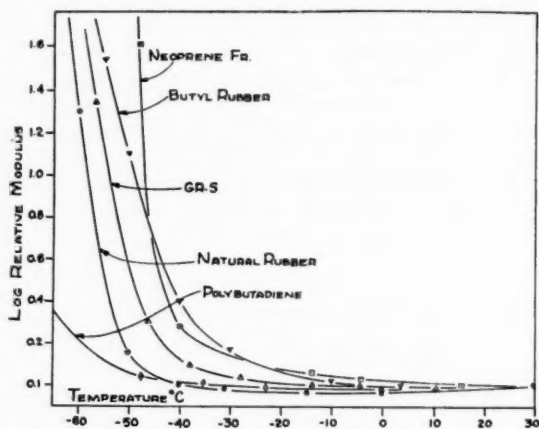


FIG. 6.—Modulus vs. temperature curve for six pure-gum elastomers, determined by single-point method. Ordinate is logarithm of ratio of the modulus to modulus at 30° C.

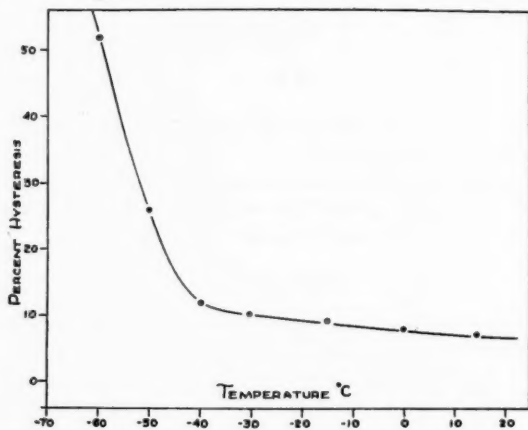


FIG. 7.—Hysteresis of a pure-gum natural-rubber stock at a number of temperatures.

degrees of its "critical" temperature, whereas a GR-S stock begins stiffening gradually just below room temperature. Yet both stocks have about the same "brittle point". The effect is even more strikingly shown by the comparison between natural rubber and Butyl. Methyl methacrylate has been shown to give the same type of modulus increase at  $71^{\circ}\text{C}^2$ . The flexibility of polybutadiene at low temperatures has been explained by Bunn<sup>9</sup> on the basis of

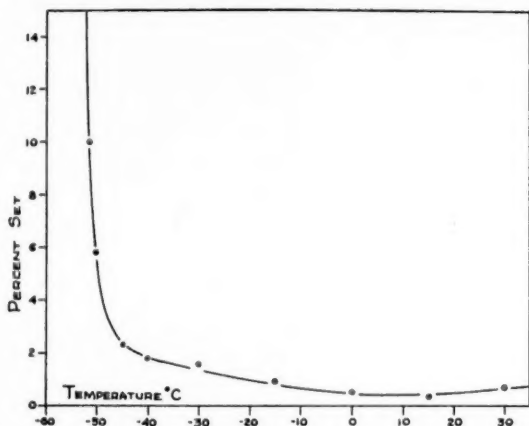


FIG. 8.—Set for a pure-gum natural-rubber stock at a number of temperatures. Set equals final elongation divided by original elongation (five minutes under 100 per cent strain, recovery after 100 seconds).

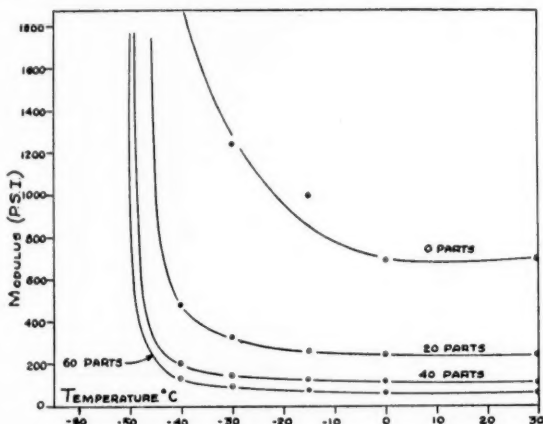


FIG. 9.—Effect of the percentage of plasticizer on the modulus vs. temperature curve. Neoprene-FR 100 parts of Thermax and indicated amounts of Circo light process oil.

lack of steric hindrance. Hysteresis and set increase approximately according to the same law as that followed by the modulus as a function of temperature. Figures 7 and 8 show typical curves. The set was measured by holding the sample under 100 per cent elongation at the temperature for five minutes, releasing it and measuring the length after 100 seconds. The values given are the ratio of the elongation remaining after 100 seconds to the initial elongation.

Figure 9 shows the effect of plasticizer on the modulus variation. Figure 10

gives the effect of reinforcing black. Plasticizers alter the shape of the relative modulus *vs.* temperature curve very little, but translate the entire curve down the temperature axis. Increasing the plasticizer content has an effect very similar to that produced by raising the temperature. Loading changes the shape of the curve in the transition range. Other interesting effects can be observed by varying the polymer. A study of the butadiene-styrene co-

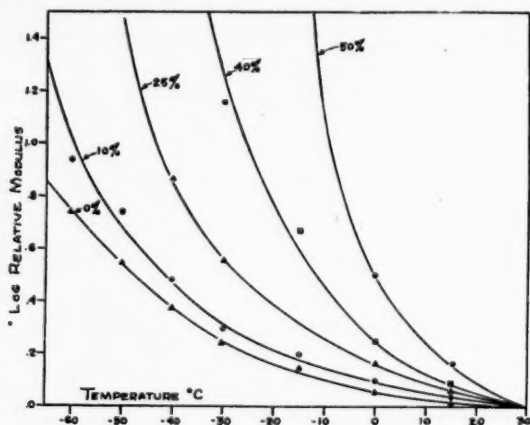


Fig. 10.—Effect of reinforcement on the modulus *vs.* temperature curve. Natural rubber with indicated proportions of Gastex (PHR).

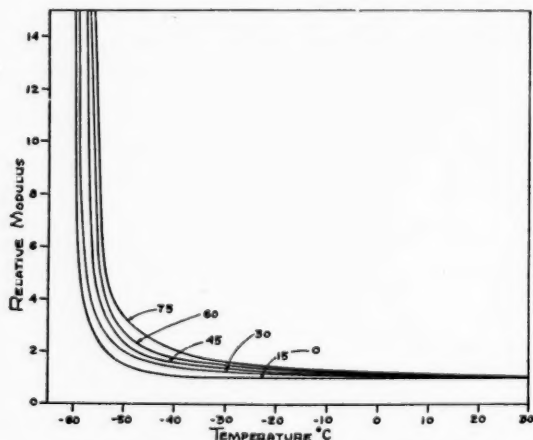


Fig. 11.—Effect of temperature on the modulus of butadiene-styrene copolymers. Figures represent percentage of styrene charged.

polymers of different compositions gives results shown in Figure 11. Increasing the styrene content of the copolymer has the combined effect of increasing the sharpness of the transition and raising the brittle point.

### RÉSUMÉ

Little has been published concerning the effect of low temperature on the elasticity of rubbers. Since in many applications this is the only property

which justifies their use, some attention must be paid to this problem. Rubbers can be characterized by the temperature at which they become brittle and by the width of the transition region. The sharpness of the transition between the elastic and the glassy states is greatest when the testing time is long compared to the molecular relaxation times. Other physical factors, such as sample shape, stress at which the modulus is calculated, and the previous history of the sample, affect the absolute nature of the elastic properties measured. A test is described which gives the values of the elastic constants at slow rates of extension, at moderate extensions, on previously flexed samples. For these conditions the superiority of gum stocks at low temperature decrease in the order: polybutadiene, natural rubber, Butyl, Neoprene-FR. The comparative values of the stocks can be changed by compounding variations. Addition of plasticizer shifts the relative modulus vs. temperature curve down the temperature scale, without producing a significant change in shape. Addition of reinforcing materials decreases the sharpness of the transition, without changing the position of the curve.

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# THEORY OF FILLER REINFORCEMENT \*

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The viscosity of colloidal suspensions and emulsions may be understood by a hydrodynamic analysis, initiated by Einstein<sup>1</sup> in 1906 and embellished by the author<sup>2</sup> and his associates. In this hydrodynamic theory the solvent is considered as a continuum. The suspended colloidal particles perturb the flow in the viscometer. This perturbation leads to an increase in the energy dissipated, which corresponds to an increase in the viscosity of the solvent. For rigid spheres suspended in a liquid, Einstein obtained the now well-known viscosity law:

$$\eta^* = \eta[1 + 2.5c] \quad (1)$$

where  $\eta^*$  and  $\eta$  are the viscosity of the emulsion and solvent, and  $c$  is the volume concentration.  $\eta^*$  thus does not depend explicitly on the radius of the suspended spheres; Equation (1) holds both for mono- and polydisperse suspensions of rigid spherical particles. Solvation may be described as a process by which the particles bind solvent and in effect "grow", causing an apparent increase in  $c$ .

Einstein's theory of viscosity gives a pattern for similar theories of other physical properties of suspensions of colloidal particles in a continuous medium whether this medium be fluid or solid. For instance, properties which may be discussed in this way include Young's modulus, thermal conductivity, and dielectric constant. Characteristic of such theories is the appearance of a property  $p^*$  of the suspension as a linear function of  $c$  for small concentrations and a power series in  $c$  for larger concentrations:

$$p^* = p[1 + \alpha_1 c + \alpha_2 c^2 + \alpha_3 c^3 + \dots] \quad (2)$$

where  $p$  designates the property of the "solvent" corresponding to  $p$ . The coefficients  $\alpha_1, \alpha_2, \alpha_3, \dots$  cannot, in general, be obtained in an elementary manner; in most cases a somewhat intricate analysis is necessary for their determination. The  $\alpha$ 's are just numerical factors for spherical filler particles but depend on the shape for asymmetric fillers. The term  $\alpha_1 c$  represents the independent action of the filler particles, the term  $\alpha_2 c^2$  the mutual interaction of pairs of particles, the term  $\alpha_3 c^3$  the mutual interaction of triplets of particles, and so on.

Here we wish to outline our theoretical treatment of viscosity, Young's modulus, and dielectric constant. For the sake of definiteness, we shall consider the reinforcement of rubber with carbon black. Our general theory will hold, however, for other systems also.

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## MODELS FOR THE RUBBER-CARBON BLACK SYSTEM

Electron-microscope studies, first carried out by Columbian Carbon Company<sup>3</sup>, revealed the spherical shape of the colloidal carbon black particles.

For the system rubber-black, three ranges of concentration of the carbon black may be distinguished.

More precisely, we define first the range within which there is no appreciable electrical conductivity ( $c$  up to about 10 per cent). In this range the colloidal carbon black spheres may be considered as suspended in a continuous rubber matrix. Figure 1 shows the model for this range. The shaded ring around the

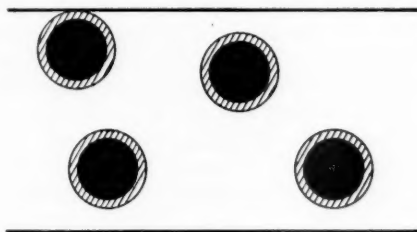


FIG. 1.—Model for the rubber-carbon black system in the first range of concentration. The white area between the black spheres represents the continuous rubber matrix. The shaded areas around the black spheres indicate the binding of rubber by the carbon black spheres.

black particles indicates the possibility of "solvation", *i.e.*, the binding of rubber by the black particles.

In the second range (up to about 30 per cent) carbon black chains develop, finally leading to a carbon black network interpenetrating the rubber network<sup>4</sup>. Figure 2 indicates the gradual development of such a conducting network. In

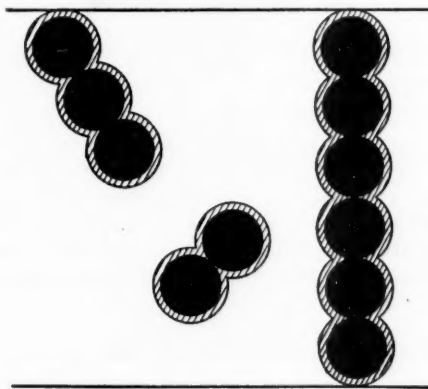


FIG. 2.—Model for the rubber-carbon black system in the second range of concentration. Chain formation may lead to a continuous conducting bridge between the boundaries of the rubber-black system. Actually, the chains are not straight, of course.

general, the chains are not straight. The rapid rise of the conductivity with concentration shows directly that there must be chains forming continuous paths between the boundaries of the rubber matrix. Then, possibly, the chain as a whole (rather than the individual spheres) will bind the rubber. As a model for such chains one may consider either a rod (as limiting case of a

prolate ellipsoid) or the set of individual spheres directly. The treatment of both models involves certain approximations, and the choice of the model depends on the nature of the problem.

The third range ( $c > 30$  per cent) may be considered as one in which carbon black is diluted by the rubber. Figure 3 illustrates the cubic (most open) packing of the spheres. The rhombohedral (closest packing) corresponds to a higher concentration.

The present paper deals chiefly with the first region. It is hoped that clarification here will lead also to a better understanding of the second and third ranges. Clearly the second range is of greatest technical importance.

The binding of rubber by pigments was apparently first pointed out by Le Blanc, Kröger, and Klotz and by Menadue. This idea was put on a firmer basis by Fielding<sup>5</sup>, and has been emphasized lately by Wiegand and his associates. The present experimental methods for the investigation of the rubber-pigment binding seem to be rather difficult and not too accurate. A somewhat simpler method will be indicated in the following two Sections.

Wiegand and associates<sup>6</sup> have advanced the idea of discrete rubber spheres surrounded by the colloidal carbon spheres. Obviously, the consequences of

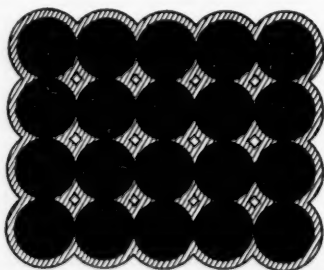


Fig. 3.—Model for the rubber-carbon black system in the third range of concentration. Cubic (most open) packing of carbon black spheres.

such an idea would be of greater importance for the second and third range of concentration than for the first range, which is the range of prime interest of the present paper. For this reason consideration of the discrete rubber theory will be deferred to a later paper. Literally taken, this theory implies in the first region a mixture of rubber and black spheres rather than a suspension of black spheres in a continuous rubber matrix. Actually, both the discrete and continuous rubber models are but different approximations for the complicated real case.

#### VISCOSITY OF THE RUBBER-CARBON BLACK SYSTEM

We have to define first what we mean by the "viscosity" of a rubber-black system. Experiment shows that a post-milled batch of the rubber-black system exhibits electrical conductivity. Thus curing is not a necessary requirement for the development of continuous paths of black spheres throughout the rubber matrix. This fact, called to the attention of the author by W. W. Vogt and J. H. Fielding, makes plausible the definition of the viscosity of the rubber by the Mooney viscosity of the milled rubber and of the viscosity of the rubber-black system by the Mooney viscosity of the post-milled rubber-black batch.

Guth and Gold<sup>7</sup> have generalized Einstein's theory and computed the coef-

ficient  $\alpha_2$  in Equation (2). Methods of calculating the interaction of a pair of spheres embedded in a moving fluid were developed by Lorentz and Smoluchowski. These methods resemble the method of images used in electrostatics. Extension of these methods leads to the viscosity law:

$$\eta^* = \eta[1 + 2.5c + 14.1c^2] \quad (3)$$

Introducing the specific viscosity  $\eta_{sp} = \eta^*/\eta - 1$ , Equation (3) may be written:

$$\eta_{sp} = 2.5c + 14.1c^2 \quad (4)$$

The viscosity law, (3) or (4), not only generalizes Einstein's law (1) for larger concentrations, but permits also a determination of the degree of solvation. Dividing Equation (4) by  $c$ , one obtains:

$$\eta_{sp}/c = 2.5 + 14.1c \quad (5)$$

Thus if one plots from experiment  $\eta_{sp}/c$  as a function of  $c$ , one should obtain a straight line, at least in the range of concentrations from 0 to about 10 per cent. The deviation from 2.5 of the intercept of this line on the  $\eta_{sp}/c$  axis measures then the degree of solvation.

Equation (4) assumes that the viscosity of the black  $\eta'$  is very large compared to the viscosity of rubber. For filler systems for which this assumption is invalid, a generalization of Einstein's theory by Taylor<sup>8</sup> leads to the relation

$$\eta^* = \eta \left[ 1 + 2.5c \left( \frac{\eta' + \frac{1}{2.5}\eta}{\eta' + \eta} \right) \right] \quad (6)$$

For  $\eta' \gg \eta$ , Equation (6) reduces to Equation (1).

For  $\eta' \ll \eta$ , as is the case with a cavity, Equation (6) reduces to:

$$\eta^* = \eta[1 + c] \quad (7)$$

The problem of the viscosity of a suspension with rod-shaped filler particles is deferred to a later paper, because of its complexity.

#### ELASTIC PROPERTIES OF THE RUBBER-CARBON BLACK SYSTEM

The model in the first range of concentration, black spheres embedded in a continuous matrix of rubber, was first applied by Rehner<sup>9</sup> to a computation of certain elastic properties. In particular he called attention to the stresses in and around the filler particles.

The computation of the change in the elastic constants of rubber by the embedded black spheres is entirely analogous to the procedure in the theory of viscosity. If a rubber-black suspension is stretched, the suspended particles perturb the stresses and strains set up in the body. This perturbation leads to an increase in the elastic energy. This in turn gives an increase in the elastic constants, *i.e.*, a stiffening of the stock. The detailed calculations are closely similar to those in the treatment of viscosity, and the final result is the same<sup>10</sup> with the Young's modulus  $E$  replacing the viscosity  $\eta$ :

$$E^* = E[1 + 2.5c + 14.1c^2] \quad (8)$$

The same relation holds also for the shear modulus  $G$ , because of the relation:

$$G = E/3 \quad (9)$$

Just as in the derivation of Equation (4), it is assumed here that Young's modulus  $E'$  for the black spheres is large compared to the modulus of rubber, an assumption which holds quite well.

According to the kinetic theory of rubber elasticity, the stress-strain relation for moderate (up to 2-300 per cent) extensions contains  $E$  only as a parameter:

$$Z = K[L - (1/L^2)]; \quad K = E/3 \quad (10)$$

Here  $Z$  is the stress per unit original cross-section and  $L$  is the relative length. In view of the elasticity law (8) it is plausible to write:

$$\begin{aligned} Z^* &= K^*[L - (1/L^2)] \\ K^* &= K[1 + 2.5c + 14.1c^2] \end{aligned} \quad (11)$$

According to this formula the embedded black spheres make the whole stress-strain curve steeper, by a factor  $K^*/K$ , depending only on the concentration. Thus stress-strain curves for varying percentages of fillers should be similar to each other. Binding can then be investigated, as in the case of viscosity. Deviations from similarity may be caused by a variety of causes (in general interdependent), such as the beginning of the network formation, change of volume on stretching, crystallization, and time effects. On the other hand, the similarity may hold at concentrations well above the range of validity of the particular  $K^*$  in Equation (11). The similarity is not bound to the theoretical stress-strain relation (10); it holds for any one-parameter family of stress-strain curves.

If the concentration increases above 10 per cent, the stiffness of the stocks increases much more rapidly than Equations (8) or (11) would predict. The reason for this is the formation of chains by the spheres. One can study this "accelerated stiffening" more nearly quantitatively by considering rodlike filler particles embedded in a continuous matrix. For this model we obtain as an analog of Equation (8):

$$E^* = E[1 + 0.67f \cdot c + 1.62f^2 \cdot c^2] \quad (12)$$

Here  $f$  is the shape factor (=length/breadth) of the rod, and we have assumed  $f \gg 1$ . For  $f \leq 1$ , one comes back to Equation (8). Equation (12) exhibits clearly the rapid increase of  $E^*$  with increasing concentration, this being, for large  $f$ , more nearly quadratic than in the case of spheres. This is in keeping with the rapid increase with concentration in the viscosity of suspensions of rodlike particles, in contrast to the slower increase for spherical particles.

It is noteworthy that stress-strain curves for varying amounts of fillers should be still similar even in the range of validity of Equation (12).

Another consequence of the elasticity theory for the rubber-black or for any other system is the influence of the tensile strength of the stress concentrations around the filler particles. J. Rehner, Jr., has called to the attention of the author a paper by Goodier<sup>11</sup>, in which this effect is treated explicitly for metals. Goodier's solution of the equations of elasticity for static equilibrium is equivalent to the solution of the corresponding viscosity problem by Taylor<sup>8</sup>, and checks with independent calculations by the author. Therefore, we simply quote his result for rigid spheres, inserting for Poisson's ratio the value 0.5 valid for rubber. In unilateral stress, a rigid sphere intensifies the stress at the poles,  $A$ ,  $A'$  from  $Z$  to  $2Z$  (cf. Figure 4) in the same direction as the applied stress (stress concentration factor = 2). The stress at the "equator" in the

same direction is reduced to a compressive stress  $(-)(1/2)Z$ . It is interesting to remark that in shear there is no intensification of the stress by rigid spheres.

An experimental check of all these theoretical conclusions has been undertaken by S. L. Dart at the Notre Dame Rubber Research Laboratory. We present here a few results. Figure 5 shows the effect of Continental semi-reinforcing carbon black in GR-S. The drawn line represents the theoretical equation (8) in the more convenient form:

$$E_{sp} = \frac{E^*}{E} - 1 = 2.5c + 14.1c^2 \quad (13)$$

The agreement with experiment is unexpectedly good, even without the as-

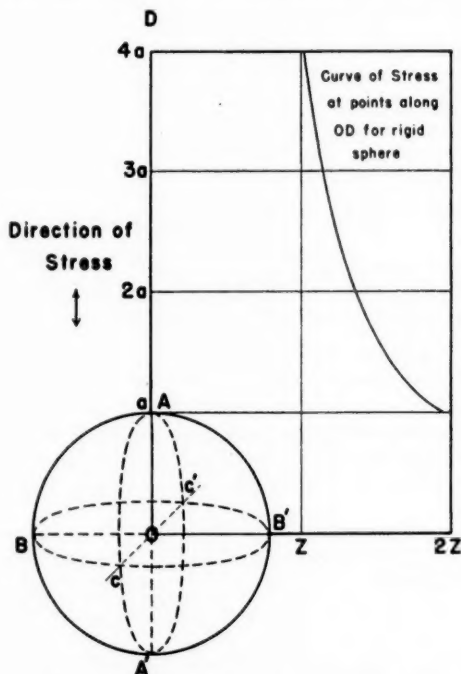


FIG. 4.—Illustration of stress-concentration around a rigid sphere.  $OD$  is the continuation of the radius  $OA$  ( $=a$ ). The stress concentration is restricted to the immediate neighborhood of the sphere. Poisson's ratio  $\mu = 0.3$  was used in this figure, but the value  $\mu = 0.5$  instead, does not make much change after Goodier<sup>11</sup>.

sumption of solvation. Figure 6 shows stress-strain curves obtained by an automatic stress-strain machine. The lower curve represents a GR-S gum stock, the upper curve a stock with 15 per cent loading. The crosses were obtained by multiplication of the lower curve by the constant factor 1.32. The deviations, 1.3 per cent of the mean, are within the experimental error.

The data of Figures 5 and 6 were measured on stocks which were not "masterbatched"; *i.e.*, they were not obtained from a masterbatch by dilution. Masterbatched stocks are being investigated. For the stocks and their physical testing we are indebted to C. S. Yoran of the Witco Chemical Company.

The expected decrease of tensile strength owing to stress concentration

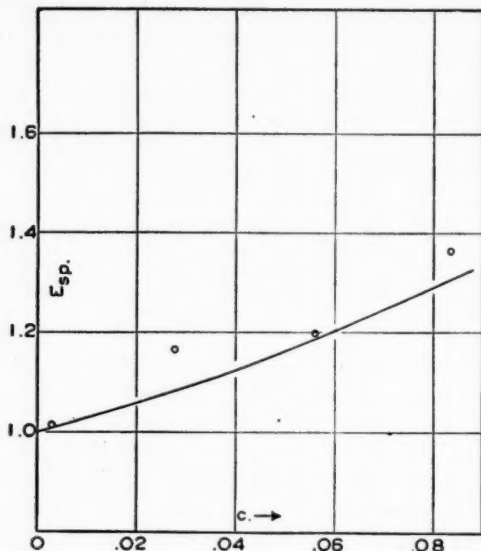


Fig. 5.—The solid curve represents the theoretical Equation (13). The circles represent experimental data for a GR-S-black system, which was not "masterbatched." The second circle is probably misplaced, owing to experimental error. The deviation from the theoretical curve of the fourth circle is in the expected direction. Note that volume concentration is roughly half of the weight concentration, used generally in the literature.

around the black particles checks roughly with observations on the same rubber-black [and rubber-calcium carbonate (Witcarb *R*)] systems, which were used to check the dependence of stiffness upon concentration. W. W. Vogt has pointed out to the author that he also found a dip in the tensile strength *vs.* concentration curve. The fact that this curve passes through a minimum

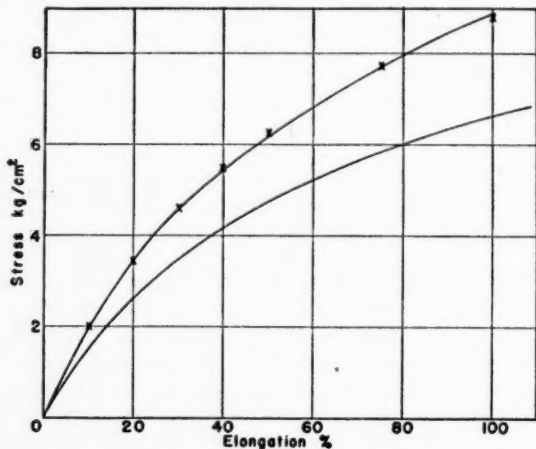


Fig. 6.—Lower curve is the stress-strain curve (for unit original cross-section) of a GR-S gum stock. The upper curve is the stress-strain curve for the same GR-S stock loaded with 15 per cent by weight Continental semireinforcing carbon black. The crosses were obtained by multiplication of the lower curve with the constant factor 1.32, thus proving the similarity of the lower and of the upper curve.

before it starts rising is not noted in the literature. Most of these curves reported start at 20 per cent weight concentration or higher, so that the minimum escaped attention.

### DIELECTRIC PROPERTIES OF THE RUBBER-FILLER SYSTEM

A discussion of the dielectric properties of the rubber-filler system may be based on the work of Rayleigh<sup>12</sup>. Rayleigh considered spheres of dielectric constant  $\epsilon'$ , arranged regularly in a cubic lattice, embedded in a matrix of the dielectric constant  $\epsilon$ . He derived for the dielectric constant  $\epsilon^*$  of this system the formula:

$$\epsilon^* = \epsilon \left[ 1 - \frac{3c}{\frac{2\epsilon + \epsilon'}{\epsilon - \epsilon'} + c - \frac{32 \cdot (3.11)^2}{5} \cdot \frac{\epsilon - \epsilon'}{(4/3)\epsilon + \epsilon'} (3/4\pi)^{10/3} \cdot e^{10/3}} \right] \quad (14)$$

For small  $c$  this somewhat unwieldy formula simplifies to the relation:

$$\epsilon^* = \epsilon \left[ 1 - \frac{\epsilon - \epsilon'}{2\epsilon + \epsilon'} \cdot 3c \right] \quad (15)$$

Equation (15) may be transformed into the form:

$$\frac{\epsilon^* - \epsilon}{\epsilon^* + 2\epsilon} = \frac{\epsilon' - \epsilon}{\epsilon' + 2\epsilon} \cdot c \quad (16)$$

if terms of higher order than  $c$  are neglected. It is clear that Equation (16) holds only in the same (linear) range of concentration in which Equation (15) is valid. The use of Equation (16) as an exact formula, as is done sometimes in the literature, has no theoretical significance. The relation Equation (15) or its equivalent was obtained by Maxwell, before Rayleigh's work. For  $\epsilon = 1$ , the Maxwell relation (15) reduces to the well-known Lorentz-Lorenz formula:

$$\frac{\epsilon^* - 1}{\epsilon^* + 2} = \frac{\epsilon' - 1}{\epsilon' + 2} \cdot c \quad (17)$$

For asymmetric filler particles a formula of the type of Equation (16) but with a shape factor  $s$  (which reduces to  $s = 2$  for a sphere):

$$\frac{\epsilon^* - \epsilon}{\epsilon^* + s\epsilon} = \frac{\epsilon' - \epsilon}{\epsilon' + s\epsilon} \cdot c \quad (18)$$

is ascribed to O. Wiener, and used also for the nonlinear range of concentrations. It is clear, however, that Equation (18) can have theoretical significance in the linear range only.

Measurements were made by Scott and McPherson<sup>13</sup> on the system rubber-calcium carbonate and Equation (18) was used for the representation of the data with  $s = 2.7$  (obtained from the nonlinear range). Though no electron microscope work was reported on the calcium carbonate used by Scott and McPherson, the electron microscope work on Witcarb *R* makes it plausible that their calcium carbonate particles were also spherical. In fact Scott and McPherson's data give  $s$  values closer to 2 in the linear range and thus check roughly Equation (15).

A full treatment of the theory of filler reinforcement with detailed derivations and more material on experimental verification will follow shortly.

## ACKNOWLEDGMENT

It is a pleasure to thank Professor Huber M. James for looking over the manuscript of this paper, and for constructive suggestions. It was planned to publish this paper jointly with him. Unfortunately, war exigencies prevented this.

## SUMMARY

For small loadings (up to about 10 per cent volume parts) colloidal carbon-black spheres may be considered as suspended in a continuous rubber matrix. In the present paper this model is generalized for ellipsoidal (including plate-like and rodlike) filler particles, and it is extended to the computation of various properties of the suspension in terms of the properties of the matrix and of the fillers. Viscosity, Young's modulus, stress-strain curve below crystallization and dielectric constant of the suspension are derived as linear functions of the volume concentration for small, and as quadratic functions for higher loadings. The stress-strain curves for varying proportions of fillers are similar. For small loadings the tensile strength first decreases because of the stress concentrations around the carbon-black spheres when the samples are stretched. The increase in tensile strength observed for greater loadings is caused by the tendency of the carbon-black spheres to form chains and, finally, a type of network. The stiffness increases with loading up to the point where the suspension becomes a dilution of carbon black by rubber. There the tensile strength decreases too. Binding of rubber by carbon black is similar to solvation. The theoretical conclusions were checked experimentally; in particular, the dependence of Young's modulus on concentration, the similarity of stress-strain curves, and the decrease of the tensile strength for small loadings. The theory of the elastic properties is very similar to the theory of Einstein on the viscosity of colloidal solutions and to Maxwell's and Rayleigh's theory of dielectric properties.

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- <sup>8</sup> Taylor, *Proc. Roy. Soc. London* **A138**, 41 (1932).
- <sup>9</sup> Rehner, *J. Applied Physics* **14**, 638 (1943). The author is indebted to J. Rehner, Jr., for interesting discussions on reinforcement.
- <sup>10</sup> The definition of  $E^*$  leading to Equation (8) is in agreement with the calculations of H. M. Smallwood, who independently obtained Equation (8) in the approximation of Einstein, i.e., without the quadratic term  $14.1c^2$ . He also undertook an experimental verification of that relation (of *J. Applied Physics* **15**, 758 (1944)). The author has considered also another simpler definition of  $E^*$  which yields the relation:  $E^* = E[1 + 3c]$  instead of  $E^* = E[1 + 2.5c]$ , as given by Equation (8). The approximations involved in the two definitions will be discussed in the detailed treatment of the reinforcement problem. In the discussion of the present paper at the Rochester meeting, H. M. Smallwood mentioned his attempt to check Einstein's viscosity law (see Equation (1) of this paper) for the rubber-black system, employing Mooney viscosities in the same way as proposed by the author in the second section of this paper.
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# THEORY OF FILLER REËNFORCEMENT \*

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In a recent paper, Rehner<sup>1</sup> discusses the stresses in the neighborhood of a spherical filler particle in rubber. He finds that all the stresses are discontinuous at the surface of the particle. His work is based on formula derived by Sezawa and Miyazaki<sup>2</sup> on the usual assumption of continuity of displacement and of the surface stresses at the spherical boundary. As the conclusions of Rehner are, therefore, inconsistent with the assumptions on which they are based, the work must contain a mathematical error at some point.

A correct solution of the problem of a spherical inclusion of any rigidity in an elastic medium under simple tension has been given by Goodier.<sup>3</sup> Goodier's paper gives formulas for the stresses at any point in the medium or inclusion when the medium is under simple tension.

Rehner considers a number of particular cases of filler particles in an elastomer. In each case the imbedded particle is much more rigid than the surrounding medium, and Poisson's ratio of the surrounding medium is very close to 0.5. When these conditions are fulfilled the stresses are the same, to a very high degree of approximation, as if the particle were entirely rigid and the medium incompressible. From Goodier's results it follows that each stress on the surface of the particle is 5/2 the similar stress at a large distance from the particle. Filler particles in elastomers or plastics are always so much more rigid than the surrounding medium that the error introduced by considering them as entirely rigid is much less than the error introduced by the use of Hooke's law.

Sezawa and Miyazaki<sup>2</sup> give a general two-dimensional solution of the equations:

$$\nabla^2 \nabla \cdot s = 0 \quad (1)$$

$$(\lambda_1 + \lambda_2) \nabla \nabla \cdot s + \lambda_2 \nabla^2 s = 0 \quad (2)$$

arising in the theory of equilibrium of elastic media and in the theory of the steady flow of viscous fluids. In the discussion of the elastic or viscous properties of a medium containing a large number of inclusions, the three-dimensional solution is much more convenient<sup>4</sup>. This can be obtained in spherical coördinates by separation of variables:

$$s = \sum_m e^{im\varphi} \sum_\gamma \left( a_{\gamma m r^\gamma} \left\{ P_{\gamma-1}^{[m]} i_r + \frac{(\gamma+2)\lambda_1 + (\gamma+4)\lambda_2}{\gamma[(\gamma-1)\lambda_1 + (\gamma-3)\lambda_2]} \right. \right. \\ \times \left[ \frac{\partial P_{\gamma-1}^{[m]}}{\partial \theta} i_\theta + \frac{im}{\sin \theta} P_{\gamma-1}^{[m]} i_\varphi \right] \Big\} \\ + b_{\gamma m r^\gamma} \left\{ P_{\gamma+1}^{[m]} i_r + \frac{1}{\gamma+1} \left[ \frac{\partial P_{\gamma+1}^{[m]}}{\partial \theta} i_\theta + \frac{im}{\sin \theta} P_{\gamma+1}^{[m]} i_\varphi \right] \right\} \\ + a_{-\gamma m r^{-\gamma}} \left\{ P_\gamma^{[m]} i_r - \frac{(\gamma-2)\lambda_1 + (\gamma-4)\lambda_2}{\gamma[(\gamma+1)\lambda_1 + (\gamma+3)\lambda_2]} \right. \\ \times \left[ \frac{\partial P_\gamma^{[m]}}{\partial \theta} i_\theta + \frac{im}{\sin \theta} P_\gamma^{[m]} i_\varphi \right] \Big\} + b_{-\gamma m r^{-\gamma}} \left\{ P_{\gamma-2}^{[m]} i_r \right. \\ \left. \left. - \frac{1}{\gamma-1} \left[ \frac{\partial P_{\gamma-2}^{[m]}}{\partial \theta} i_\theta + \frac{im}{\sin \theta} P_{\gamma-2}^{[m]} i_\varphi \right] \right\} \right) \quad (3)$$

\* Reprinted from the *Journal of Applied Physics*, Vol. 16, No. 1, page 55, January 1945.

$m$  integral,  $\gamma$  integral  $> 0$ ,  $P_\gamma^{lm} = P_\gamma^{lm}(\cos \theta)$  = Legendre polynomial of order  $\gamma$ ,  $|m|$  and argument  $\cos \theta$ .

For the usual boundary conditions at infinity:

$$s \rightarrow Axi + Byj + Czk \quad (4)$$

and boundary conditions in the finite region independent of angle, the solution becomes:

$$\begin{aligned} s &= \left[ \frac{1}{3}(A + B + C)(r + b_{-2}r^{-2}) + (r + c_{-2}r^{-2} + c_{-4}r^{-4})M(\theta, \varphi) \right] i_r \\ &\quad + \frac{1}{2} \left( r + \frac{2\lambda_2}{3\lambda_1 + 5\lambda_2} c_{-2}r^{-2} - \frac{2}{3} c_{-4}r^{-4} \right) \\ &\quad \times \left( \frac{\partial M}{\partial \theta}(\theta, \varphi) i_\theta + \frac{1}{\sin \theta} \frac{\partial M}{\partial \varphi}(\theta, \varphi) i_\varphi \right) \\ s &= [a_1r + (c_1r + c_3r^3)M(\theta, \varphi)] i_r \\ &\quad + \frac{1}{2} \left( c_1r + \frac{5\lambda_1 + 7\lambda_2}{3\lambda_1} c_3r^3 \right) \left( \frac{\partial M}{\partial \theta} i_\theta + \frac{1}{\sin \theta} \frac{\partial M}{\partial \varphi} i_\varphi \right) \\ M &= \frac{1}{3}(A + B - 2C)P_2(\cos \theta) \\ &\quad + (1/12)(A - B)P_2^2(\cos \theta)(e^{2i\varphi} + e^{-2i\varphi}) \\ &= A \sin^2 \theta \cos^2 \varphi + B \sin^2 \theta \sin^2 \varphi + C \cos^2 \theta - \frac{1}{3}(A + B + C) \end{aligned} \quad (5)$$

The undetermined constants are fixed by the boundary conditions in the finite region.

In an elastic medium of bulk modulus  $\lambda_1$ , modulus of rigidity  $\lambda_2$ , in which there is a spherical particle of radius  $R$ , with Lamé's constants  $\lambda_1'$  and  $\lambda_2'$ , at the origin of coördinates, the constants have the values, on the usual assumption of single-valued displacements and single-valued stresses on the surface of the particle:

$$\begin{aligned} b_{-2} &= (3\lambda_1 + 2\lambda_2 - 3\lambda_2' - 2\lambda_2')(4\lambda_2 + 3\lambda_1' + 2\lambda_2')^{-1}R^{-1} \\ c_{-2} &= -5(3\lambda_1 + 5\lambda_2)DR^{-1} \\ c_{-4} &= +9(\lambda_1 + \lambda_2)DR^{-3} \\ a_1 &= (A + B + C)(\lambda_1 + \lambda_2)(4\lambda_2 + 3\lambda_1' + 2\lambda_2')^{-1} \\ c_1 &= 15\lambda_2(\lambda_1 + 2\lambda_2)D(\lambda_2' - \lambda_2)^{-1} \\ c_3 &= 0 \\ D &= [2\lambda_2'(3\lambda_1 + 8\lambda_2) + \lambda_2(9\lambda_1 + 14\lambda_2)]^{-1}(\lambda_2' - \lambda_2) \end{aligned} \quad (6)$$

When  $A = B = -\sigma C$ ,  $\sigma$  = Poisson's ratio  $= \lambda_1/2(\lambda_1 + \lambda_2)$ , the stresses calculated from these solutions are those given by Goodier. When  $\lambda_1 \rightarrow \infty$ ,  $\lambda_2 = \mu$ , the coefficient of viscosity,  $\lambda_1'$  and  $\lambda_2' \rightarrow \infty$ , these solutions reduce to those given by Einstein<sup>4</sup> in Cartesian coördinates. Einstein's method of averaging over the particles can be used to determine approximately the elastic properties of a filled medium in which the filler particles are widely separated.

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- <sup>2</sup> Sezawa and Miyazaki, *J. Soc. Mech. Eng. Tokyo* **31**, 625 (1928).
- <sup>3</sup> Goodier, *J. Applied Mech.* **1**, 39 (1933). This paper was brought to the writer's attention by Rehner. When his paper on the subject was published, Rehner was unaware of Goodier's work.
- <sup>4</sup> Einstein, *Ann. Physik* **19**, 289 (1906); **34**, 591 (1911).

## THE PROÖXYGENIC EFFECT. CHANGES WHICH TAKE PLACE IN VULCANIZED RUBBER \*

PAUL CHOVIN

The autoöxidation of rubber is sensitive to the action of catalysis; anti-oxygenic compounds are antagonistic to the process and retard its progress; proöxygenic compounds on the contrary promote autoöxidation, and in their presence the effects of autoöxidation are evident sooner. In the present paper, experiments are described, the object of which was to study the action of a few typical proöxygenic compounds on rubber hydrocarbon.

Among the substances which accelerate the action of oxygen, certain salts of copper, iron, cobalt, and manganese are known to be very active. Various organic derivatives of these metals were studied in the present work, including (1) copper acetylacetonate, oleate, linoleate, sulforicinoleate, elaidate, stearate, enanthate, pelargonate, hendecenate, erucate, and diethylthioneethiolcarbamate; (2) iron acetylacetonate, oleate, linoleate, sulforicinoleate, and pelargonate, and the dibenzoylmethane derivative of iron; (3) cobaltous oleate, linoleate and sulforicinoleate, and cobaltic acetylacetonate; (4) manganous oleate, linoleate, sulforicinoleate and pelargonate, and manganic acetylacetonate. A study was also made of certain more complex metal derivatives, including salts of the dithizone of cupferron, of mercaptobenzothiazole, of  $\alpha$ -nitroso- $\beta$ -naphthol, of benzyldioxime, etc. The method followed involved two steps: (1) incorporation of a predetermined percentage of a proöxygenic metal compound into samples of vulcanized rubber, (2) estimation of the acceleration of autoöxidation induced by the particular proöxygenic compound. In the first step, the rubber sample was cut into small cubical pieces 2-3 mm. on a side, and these were placed in a chloroform solution of the particular salt under investigation. The average content of proöxygenic compound which was absorbed was about 0.1 per cent. The swelling of the rubber in the solution was the determinant factor in the total amount of proöxygenic compound and solvent which were absorbed.

The final step was to remove the solvent by heating the samples in an oven for 2 hours at 70° C or in a vacuum for 15 minutes at 100° C, so that only the proöxygenic agent remained in the rubber. Under these conditions the sample is not in all cases thoroughly impregnated, but this does not influence appreciably the reproducibility of an experiment or the comparative results in determining the acceleration of autoöxidation.

The second step, i.e., the determination of the acceleration of autoöxidation, involves the use of the manometer of Dufraisse<sup>1</sup>. The rate of autoöxidation of a sample impregnated with a proöxygenic compound is merely compared with the rate of autoöxidation of a control sample.

In what follows, the *coefficient of acceleration* is defined arbitrarily as the quotient of the rate of autoöxidation of an impregnated sample at the end of the

\* Translated from RUBBER CHEMISTRY AND TECHNOLOGY from *Comptes Rendus Hebdomadaires des Sciences de l'Académie des Sciences*, Vol. 212, No. 19, pages 797-800, May 12, 1941.

fifth minute divided by the constant rate of autooxidation of the control sample, determined at the end of its induction period (an induction period is always observed in a control sample). The definition finds its justification in the fact that not only is there generally no appreciable period of induction in the case of samples impregnated with a proöxygenic compound, but that the curves representing the rise of the mercury column as a function of time show in most cases a rapidly diminishing slope after a short period of time, *i.e.*, of the order of 5 to 10 minutes. This phenomenon is to be attributed to the action of oxygen on the impregnated cubes of the rubber sample, an action which is manifest in the formation of a film of oxidized material, which melts and then forms a varnish surface only slightly permeable to oxygen. It follows that, as the consumption of oxygen progresses, its rate becomes progressively less rapid as the result of this purely mechanical effect. This phenomenon explains the increased concavity of the curves.

The coefficients of acceleration determined in this way give valuable information on the activities of various proöxygenic compounds, but these coefficients should be interpreted with considerable reserve. It is, in fact, well known that the phenomena of autooxidation in general frequently show irregularities<sup>2</sup>, particularly in the case of a substance as complex as rubber. Conditions which seem to be identical, *e.g.*, the same composition of mixtures, the same time of mixing, the same time and temperature of vulcanization, etc., lead, nevertheless, when no proöxygenic compound is present, to degrees of initial oxidizability which vary within rather wide limits. A study of the influence of positive catalysts of autooxidation on the behavior under these conditions has shown: (1) that for a given proöxygenic compound and different sets of samples, the greater the initial autooxidizability of the sample, the higher is the coefficient of acceleration, and (2) that the ratio of the coefficients of acceleration induced by two different proöxygenic compounds is not the same for different rubber samples, in fact there is no rule as to whether the ratio will increase or decrease from sample to sample.

Fairly large differences are, therefore, likely to be found in the results of such measurements under a given set of conditions. However, in view of the considerable effects of metal compounds on the rate of autooxidation, relatively small differences should not be regarded as playing any significant part in the general conclusions which can be drawn from such work.

The measurements which are given below in parentheses represent the mean coefficients of acceleration, determined at 80° C, of a rubber sample containing no antioxygenic compound.

The most active salts were, on the one hand, cobalt sulforicinoleate (65), manganese pelargonate (50), iron pelargonate (12), copper oleate (14), copper sulforicinoleate (10), and copper pelargonate (7). In a different sample whose initial autooxidizability was approximately one and one-half times that of the previous sample, the most active salts were manganese linoleate (82), ferric acetylacetonate (72), cobalt acetylacetonate (63), and manganic acetylacetonate (51). The other salts, particularly the complex derivatives, in which the effect of the metals is more or less obscured, were found to be far less active. It is worthy of note that copper diethylthionethiolcarbamate is slightly proöxygenic at 80° C, but slightly antioxygenic at 120° C.

It seemed of interest to test these catalysts in binary mixtures and in ternary mixtures, because of the possibilities of mutual reënforcement of the catalytic action, a phenomenon incorrectly called promoting action.

In the study of binary mixtures, copper pelargonate, iron pelargonate, manganese pelargonate and cobalt sulforicinoleate were chosen. Each pair was tested in different proportions, but in each case in such percentage that the total metal content was 0.1 per cent of the rubber. Only the iron-cobalt combination in the ratio of 1:1 showed an activity (67) slightly superior to that of the more active of the two components. In the case of all other possible combinations of four constituents, the activity of binary mixtures was lower than the activity of the more active component mixture, and in some cases the activity of the binary mixture was even lower than the activity of the less active of its components.

Among the ternary mixtures investigated, which included iron pelargonate, manganese pelargonate, and cobalt sulforicinoleate, each with a total metal content of 1 per cent based on the rubber, only one mixture, *viz.*, that having an iron-manganese-cobalt ratio of 3:1:1, was found to have an activity (73) which, without being much greater than that of the more active component, Co (65), at least exceeded it appreciably. Triangular representation gave ample evidence that the field of ternary mixtures was explored in a sufficiently methodical way to make it certain that no mixtures of greater activity escaped detection.

In conclusion it is evident that, in the case of the autooxidation of rubber, a mutual increase in the activity of catalysts is far from attaining the very high proportions encountered with certain classic mixtures, such, for example, as hopcalite, which shows a remarkably high degree of activity, particularly in autooxidation reactions.

#### REFERENCES

- <sup>1</sup> For a bibliography on the subject see Dufraisse, "The Chemistry and Technology of Rubber," Edited by Davis and Blake, Reinhold Publishing Corp., New York, 1937, p. 440.
- <sup>2</sup> Cf. Dufraisse and Chovin, "Handbuch der Katalyse," G. M. Schwab, Vienna, 1940, Chap. 2, "Katalyse in Lösungen," p. 388, "Negative catalysis in the liquid phase and solid phase."

# PHOTOVULCANIZATION

## A STUDY OF THE PRODUCTS OF THE ACTION OF LIGHT ON RUBBER UNDER CONDITIONS PRECLUDING OR RESTRICTING OXIDATIVE DEGRADATION \*

HENRY P. STEVENS

### INTRODUCTION

There are numerous references in the literature to the action of light on rubber, either in massive form, in solution, or dispersed as a latex. This communication deals only with the first of these and in the substantially plastic form of milled crepe, either as calendered sheet or cut sheet. There are disadvantages in working with unmilled rubber, particularly latex films, as the variable elastic properties of the original material are apt to mask any improvement, *i.e.*, increased modulus or other tensile properties developed by irradiation.

When milled sheeted rubber is exposed to sunlight or otherwise irradiated, the surface softens and becomes tacky. On further exposure it hardens, and the inelastic oxidized surface layer usually crazes. An increase in weight of 2.9 per cent took place in 65 days insolation of a 1 mm. thick sheet. In a solvent such as benzene, this product swells and is only partially soluble. Asano<sup>1</sup> showed that insolubilization also took place if the rubber were exposed in an inert gas. Garner<sup>2</sup> exposed tubes containing raw rubber to ultraviolet radiation both in nitrogen and carbon dioxide for 40 hours with special precautions to ensure absence of air, particularly traces occluded on the surface of the rubber, and obtained "much insoluble rubber". He does not state that the raw rubber was milled, but a parallel experiment was made by irradiation of crepe purified by precipitation with alcohol from a toluene solution. This, on analysis, after irradiation, gave figures substantially identical with those obtained before treatment. The irradiated rubber was not tacky. As might be expected the introduction of a small amount of oxygen into the tube resulted in a tacky rubber, as in the case of exposure in air. This behavior corresponds to the effect produced by insolation of rubber sols. The formation of a gel in the absence or restricted presence of air takes place as a result of the insolubilization of the rubber in solution<sup>3</sup>.

### ISOLATION OF DRY RUBBER

The writer has recently published the results of swelling and solubility tests on various raw and purified rubbers insolated in air and in vacuo<sup>4</sup>. With the rubber insolated in air the effect produced by light is complicated by the oxidative degradation which takes place. The absorption of oxygen may be restricted or prevented by the use of certain reagents or sensitizers, but for working with 'pure' rubber sheet it is necessary to avoid oxidative effects by exposure in vacuo or in an inert gas. Under these conditions not only is milled

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sheeted rubber without any sulfur or other agent rendered largely insoluble, but it also regains a part of the elasticity which it had lost in the milling process. Stress-strain curves for a number of insulated specimens exposed to sunlight for varying periods in sealed exhausted tubes are given in Figure 1, including

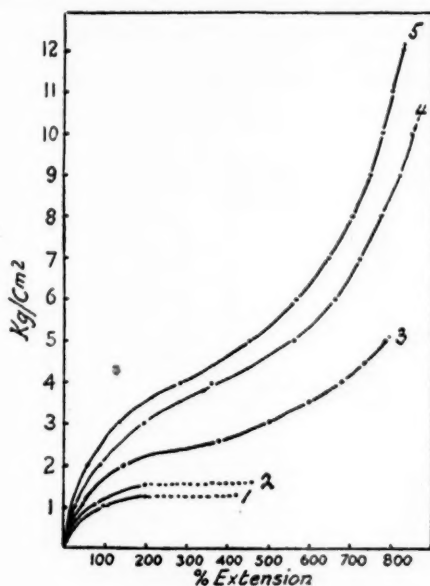


FIG. 1.—Photovulcanization of milled rubber without agents in vacuo. The dots represent observations and the junctions with the broken lines indicate yield-points from whence the specimen continues to elongate without application of increased tension.

that of the sheet before insulation. The corresponding swelling and solubility tests, together with the load required to elongate 600 per cent, are given in Table I. 4 and 5 swelled in benzene to moderate extent and the 18 per cent

TABLE I  
PROPERTIES OF VULCANIZATES OBTAINED BY INSULATION OF MILLED RUBBER BY ITSELF IN VACUO. CORRESPONDS TO FIGURE 1

Period of exposure	Load at 600% extension (kg. per sq. cm.)	Swelling index	Proportion soluble
1. Control—untreated	1.3	Completely soluble	—
2. Insolated 5 hours in quartz tube	1.6	“	—
3. Insolated 4 months in glass tube	3.5	49.7	.41
4. Insolated 1 year in glass tube	5.4	23.5	.18
5. Insolated 1 year in glass tube	6.3	22.4	.18

soluble includes 3 to 5 per cent of nonhydrocarbon components, so the actual amount of hydrocarbon dissolved must be reduced by this amount.

## PART 1.—THERMAL AND COLD CURES

### PHYSICAL BEHAVIOR OF SLIGHTLY VULCANIZED RUBBER

A search in the literature failed to discover a systematic physical or chemical examination of slightly vulcanized rubber; and as data were required for

comparison with the results of tests on photochemically vulcanized rubber, Part I comprises a few experiments made with rubber-sulfur mixes cured progressively and with sulfur-chloride vulcanized rubber. Specimens of the stress-strain curves obtained are shown in Figures 2-5. These reveal a marked difference in the shape of the curves between the heat-cured and cold-cured rubber, respectively. The heat-cured, Figures 2 and 3, give the same type of curve for all degrees of vulcanization. At the early stage, as with milled unvulcanized sheet, the rubber exhibits a yield point at a relatively small load, at which stage it continues to stretch, as indicated by the broken lines, without further

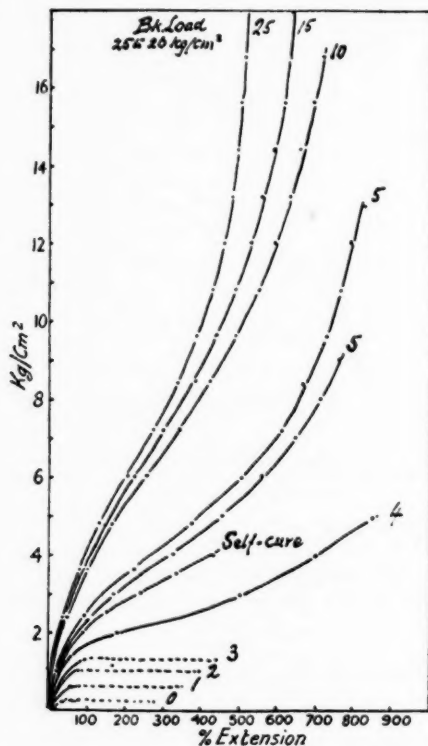


Fig. 2.—Thermal vulcanization. Effect of period of cure. Corresponds to Table II. The figures indicate minutes cure.

additional loading, until it breaks. The figures (Table II) give the percentage of combined sulfur for each period of heating. When the percentage of combined sulfur reached 0.22 per cent (4. Figure 2) the specimen no longer showed a yield point with increasing load, but gave the normal type of stress-strain curve for a vulcanized rubber. This, of course, is somewhat conditioned by the temperature and rate of loading. The specimens show the usual progressive improvement with time of cure. The two curves for the 5-minute cure (Figure 2 and Table II) are duplicates, specimens 1 to 5 and 5 to 25 minutes having been cured in separate batches. The curve marked "self-cure" was obtained at a later date after the sheets stored in the dark had begun to vul-

canize spontaneously. Figure 3 depicts a series of tests with different rates of loading and temperature. It is seen that the shape of the curve is not materially altered by a change of temperature or rate of loading during testing. There seems to be no doubt, if Figure 1 be compared with Figures 2 and 3, that rubber photovulcanized without sulfur or other agent is physically indistinguishable from that thermally vulcanized with sulfur; and that as vulcanization proceeds they both pass through the same stages.

In contrast to the thermally vulcanized, undervulcanized cold-cured rubbers

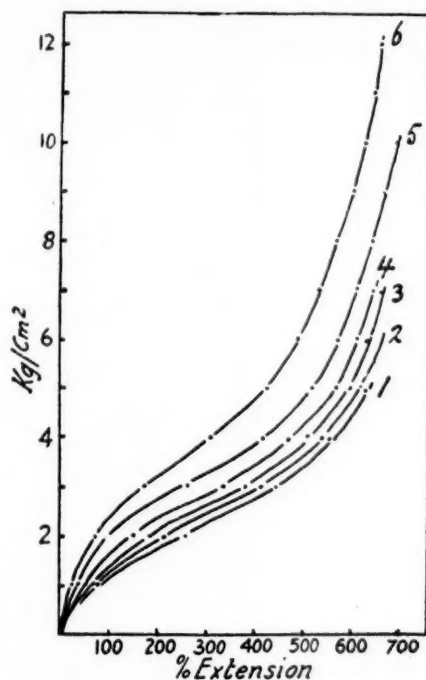


Fig. 3.—Thermal vulcanization. Effect of rate of loading and temperature.

	Rate kg./cm <sup>2</sup> /sec.	Temperature
1	0.003	22°
2	0.008	22°
3	0.016	22°
4	0.033	22°
5	0.100	22°
6	0.100	17.5°

give a different type of curve, as will be seen from Figures 4 and 5, which refer to a series of vapor cures varying from 1 to 30 minutes treatment. The curves for all cures (Figure 4) except the last (30 minutes) show a sharp inflection at an elongation of about 400 per cent. The behavior of rubber vulcanized by the vapor cure to a low degree, is very dependent on external conditions, particularly on temperature and rate of loading, more so than thermally cured. The 4 minutes specimen began stretching rapidly at an elongation of 250 per cent and with a load of 1.4 kg., and attained an elongation of 840 per cent without additional load, but did not break at this stage under the conditions

of the experiment as did the lower cure (2 minutes). On further loading it stretched still more, breaking at a high elongation of 1,200 per cent. In this respect it resembles racked rubber. The 8-minute cure shows a very marked bulge at an elongation of 350 per cent to 450 per cent, after which it continues to stretch normally. The 16-minute cure shows a similar but less pronounced "flow bulge", which is absent from the 30-minute cure. The curves shown in Figure 5 correspond to different rates of loading, and the pronounced bulges at about 400 per cent elongation are again prominent. The layout of the

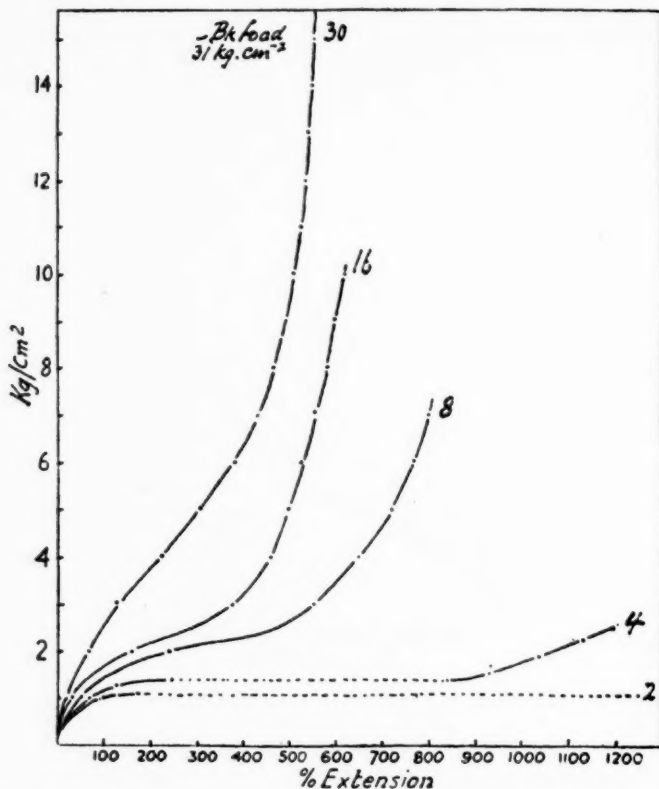


Fig. 4.—Sulfur chloride vapor cures. The figures 2–30 indicate minutes exposure to the vapor.

curves varies somewhat, but the rate of loading does not alter their character. Cold cures in benzene solution gave similar results.

#### PHOTOVULCANIZATION CONTRASTED WITH THERMAL VULCANIZATION AND COLD CURES

It may be conjectured that this pronounced plastic behavior at a stage in the stretching of undervulcanized cold-cured rubber, and which is characteristic of both liquid and vapor cure, depends on the circumstance that by these methods of operation vulcanization is not uniform throughout the thickness of the sheet, but is concentrated in the surfaces because the vulcanizing agent

penetrates slowly and incompletely. It reacts as it penetrates, so that the makeup of such a sheet will be a vulcanized outer film on both sides, with many of the inner layers only slightly vulcanized or not at all. Similar conditions may be expected to apply to irradiated rubber sheets, according as vulcanization is dependent on the penetration of the rays and their absorption by the rubber, but penetration will be from one face only, instead of both faces as in cold-cure processes. The curves in Figure 1 are seen, however, to resemble the heat vulcanizates (Figures 2 and 3) rather than the cold-cures (Figures 4 and 5). This indicates a ready penetration by the rays and a

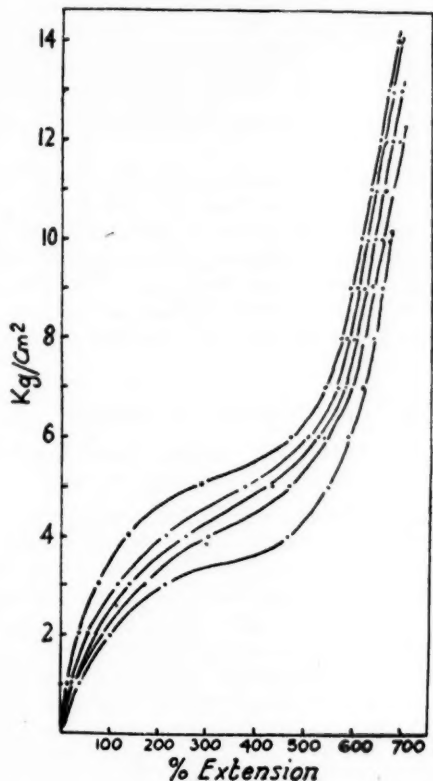


Fig. 5.—Sulfur chloride vapor cures. Rate of loading, 0.1 kg. to 0.002 kg. cm<sup>-2</sup>. sec<sup>-1</sup>.

uniform vulcanization in depth. The curves (Figure 1) of photovulcanized rubber correspond almost exactly with those of the thermally vulcanized specimens. These data, in conjunction with the solubility and swelling properties (Tables I and II) and also the greater resistance to hardening at low temperatures, indicate that the effect of insolation alone on rubber is to produce a small degree of vulcanization, which effect is of uniform distribution and penetration, indistinguishable from that obtained by thermal vulcanization with the agency of sulfur and accelerators, and is not concentrated in either surface.

Although the modulus and tensile strength of slightly vulcanized rubber is

TABLE II  
PROPERTIES OF THERMAL VULCANIZATES. CORRESPONDS TO FIGURE 2

Minutes cure	Load at 600% extension (kg. per sq. cm.)	Swelling index	Proportion soluble	Combined sulfur (percentage)
0	* 0.2	Mainly soluble	—	—
1	* 0.6	" "	—	0.04
2	* 1.0	" "	—	0.13
3	* 1.3	" "	—	0.17
4	3.4	" "	—	0.22
Self cure	* 5.0	22.0	0.22	0.28
5	6.5	—	—	0.25
5	7.1	19.0	0.13	0.37
10	12.1	15.8	0.10	0.39
15	16.2	12.2	0.08	0.44
25	*28.0	8.4	0.06	0.53

\* Figures obtained by interpolation.

low, whether attained thermally or photochemically, it will be noted that the extension at break is high, usually not less than 700 to 800 per cent, *i.e.*, not so far short of the 950–1000 per cent given by well vulcanized soft rubber without loading. The recovery after stretching of these lightly vulcanized rubbers is quite good and not far removed from that of a well vulcanized soft rubber, provided that the initial stages of vulcanization are passed and the rubber possesses a tensile of 8 to 15 kg. per sq. cm. See also various graphs referred to in the next section.

## PART 2.—PHOTOVULCANIZATES

### INSOLATION OF DRY RUBBER DUSTED WITH SENSITIZERS (PHOTOVULCANIZING AGENTS) IN AIR

If a sheet of milled rubber be exposed in air to sunlight for a few hours on a glass plate, both surfaces become tacky. On this account the under side adheres so firmly to the glass that it cannot be removed. As this close contact excludes further free access of air, only the upper surface continues to oxidize and harden so that it eventually crazes. The swelling and insolubility in solvents of an air-insolated specimen are of the same order as of a vacuum-insolated specimen exposed simultaneously; but in contact with air, the physical properties have deteriorated. It appears that insolation of milled rubber tends to insolubility and restricted swelling, both in the presence and absence of air. The product in the former case is softer and weaker than the original milled sheet and more soluble in acetone. It may be concluded that a change, which may be termed photovulcanization, takes place in both cases, but in the presence of air the accompanying improvement in physical properties is masked by the formation of oxidation products produced by oxidative photolysis. It was deemed of interest to discover if the oxidation could be inhibited by chemical means, and with this object in view powdered hydroquinone was rubbed well into both surfaces of a clean sheet of rubber recently with benzene. It was found to have a very slight effect as an oxygen inhibitor, or none at all. Other reagents were tried with a variety of results, and some gave good vulcanized products, even in the presence of air. They fall into three classes. Firstly, as examples, *p*-phenylenediamine, alizarin, eosin and phenolphthalein, which have no protective action. Secondly, benzidine, aurin, hydroquinone and others which prevent adhesion to the glass but otherwise have little or no

effect on the rubber. Thirdly, reagents which bring about an improvement in physical properties. These include sulfur, photogelling agents and to a lesser extent some organic accelerators in the absence of sulfur, particularly, mercaptobenzothiazole, thiocarbanilide and the zinc and sodium salts of diethyldithio-

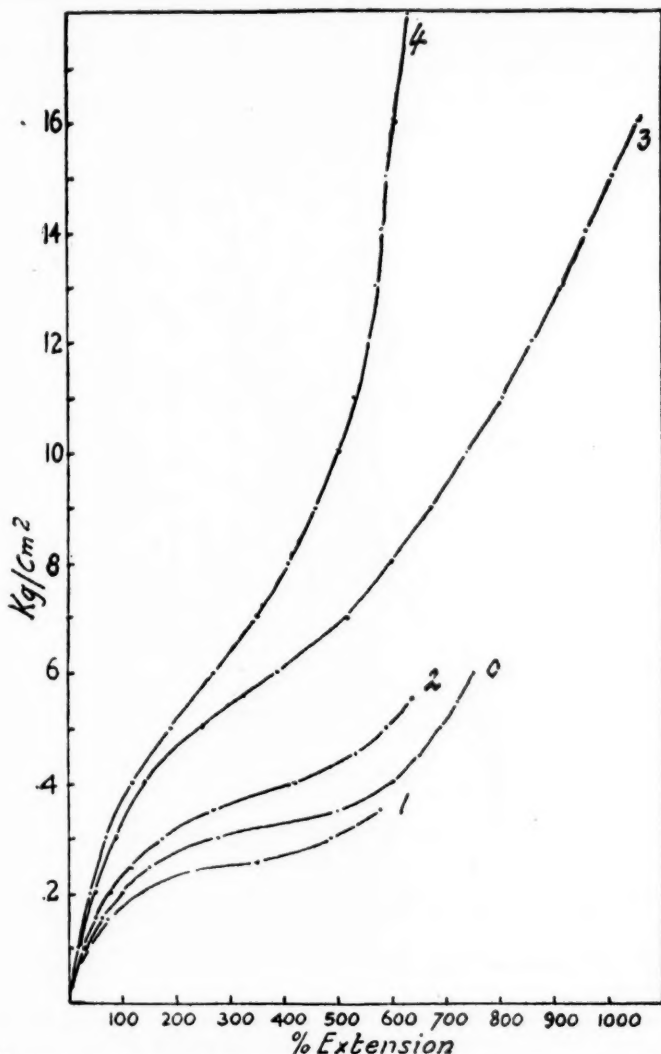


FIG. 6.—Insolation of milled rubber for four months in isobutane, the under surfaces dusted with powdered reagents. For significance of numbering, see Table III (1).

carbamic acid. Not all vulcanization accelerators are vulcanization promoters or photo-agents; thus, polymerization products of ethyldeneaniline and aldehydeamines are either inactive or may even promote oxidation, as indicated by the early development of adhesiveness. Similarly diphenylguanidine causes

premature softening, as would be expected from its appreciable solubility in rubber<sup>5</sup> and its action as a softener on the mill. Thiocarbamide and formaldehydeaniline prevent adhesion when the rubber sheet is insolated on a glass plate. The best vulcanizates were obtained by insolation in the presence of those activators or sensitizers which promote photogelling of a rubber sol, *i.e.*, CO compounds, such as aromatic aldehydes, ketones, quinones and their chlorinated derivatives. Parallel thermal vulcanization with chlorinated quinones has been described by Fisher<sup>6</sup>, but the physical properties are much inferior to sulfur vulcanizates. Good results are also obtained by insolation

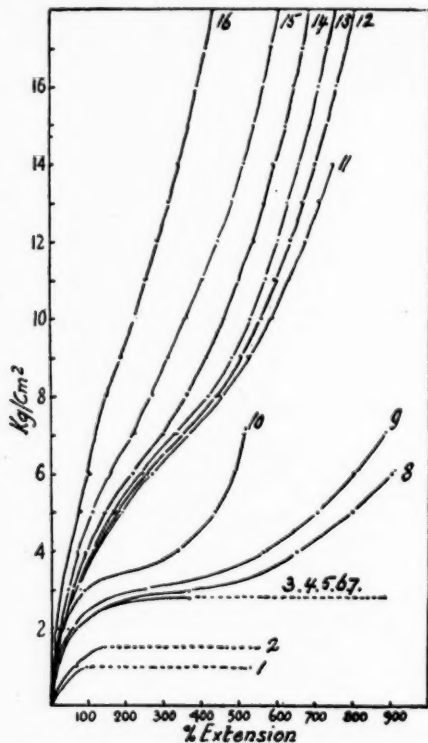


FIG. 7.—Insolation of surface treated milled rubber in vacuo for four months. The graph does not show the end points of 12 to 16. For significance of numbering, see Table III (2).

with sulfur as in thermal vulcanization, but no better than those obtained with CO compounds.

When the insolation is carried out in inert gas or in vacuo there is, of course, no sign of softening or stickiness such as is induced by oxidation, even in the presence of diphenylguanidine or the other substances mentioned. In the earlier experiments the rubber before insolation was coated on both sides with sensitizer, but it was found that much the same results were obtained by coating the upper surface only and, generally, better results by coating the under surface only. Mill mixes of rubber, sulfur or quinones and other activators are quite unsuitable for exposure. A thin vulcanized skin forms on the upper surface and the greater part of the rubber beneath remains unaltered. It is

evident that all these observations are consistent with the optical opacity of the sulfur and (or) activator which absorbs the active rays and protects the rubber below, that is, these reagents may be said to act as internal filters. The same process probably accounts for the retardation or absence of gelling of irradiated rubber sols which has been observed with sulfur and zinc oxide<sup>7</sup>. Figures 8, 10 and 11 give results obtained in the presence of air and, Figures 6, 7 and 9 in the absence of air. Table III gives the corresponding data. With thin sheets in the presence of active reagent, there is no indication of softening

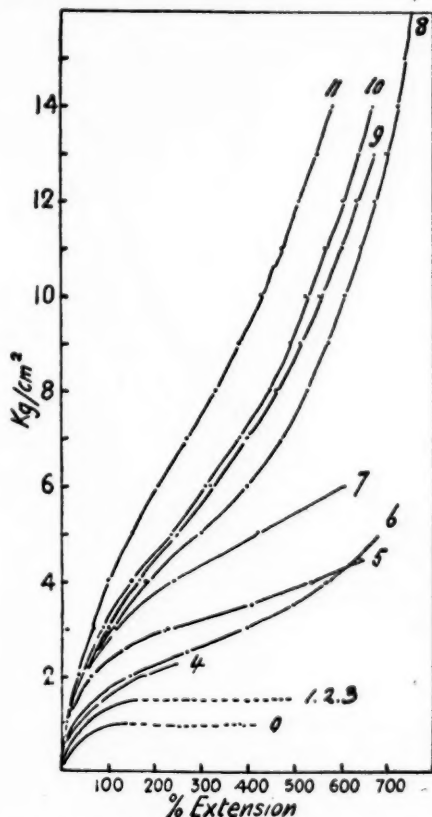


FIG. 8.—Insolation of surface treated milled rubber in air for three sunny days. For significance of numbering, see Table III (3).

or stickiness developing on the upper surface directly exposed to the light when the undersurface only is coated with the reagent, even when the photovulcanization takes place with free access of air.

#### INSOLATION IN THE ABSENCE OF AIR

It will be seen that in all experiments in the absence of air similar results were obtained. There was no stickiness in any insolated specimen, even those which showed no improvement in tensile properties. The tensile figures of specimens insolated in vacuo given in the accompanying data are higher than

those in isobutane, but strict comparison is not possible, as the period of exposure cannot be allowed for unless specimens are insulated simultaneously; even then it is difficult to ensure uniform illumination. The maximum figures are not reached under the conditions under which the tests are made, as straight strips and plain grips were used (see under Experimental). A few tests with strips cut dumb-bell shaped gave appreciably higher figures. It seems probable that still higher tensile figures would be obtained under the most suitable conditions and sufficiently prolonged irradiation or insolation. As in thermal vulcanization a large number of trial cures must be made to obtain optimum

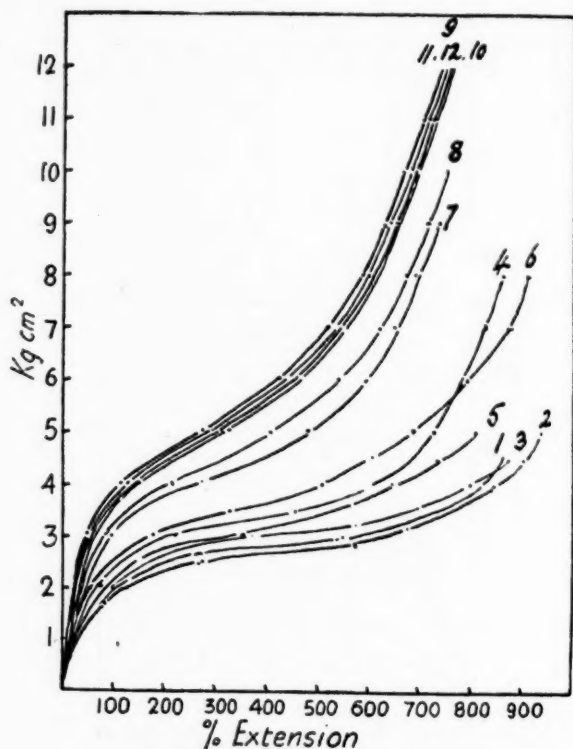


FIG. 9.—Insolation of milled rubber in isobutane, the under surfaces dusted with sulfur, sulfur and accelerators and accelerators alone. For significance of numbering, see Table III (4).

results, and such take much longer and are more difficult with photovulcanization. The rubber specimens sensitized with anthraquinone, dichloranthraquinone, chloranil and sulfur gave approximately the same breaking load of 24 kg. per sq. cm., the xanthone a little less, and the others as indicated on the graph (Figure 7). It will be seen that a number of reagents are without appreciable effect, or even retard photovulcanization.

#### INSOLATION IN AIR

Those sensitizers or vulcanizing agents which give good results in vacuo give lower tensile figures insulated in air, and become weak and brittle without

developing the maximum obtained in vacuo. Figure 8 illustrates the type of curve obtained by insolation in air. They are similar to those given by the rubber insolation in vacuo or inert gas. Longer exposure in air did not improve them, and the figures shown after three sunny days insolation were in almost every case better than those obtained after three weeks' insolation, by which time the tensile strength had fallen in some cases to one-tenth of the previous figure. Photovulcanization promoted by sensitizers or agents including sulfur, when air is present, may therefore easily result in an overcure. This is charac-

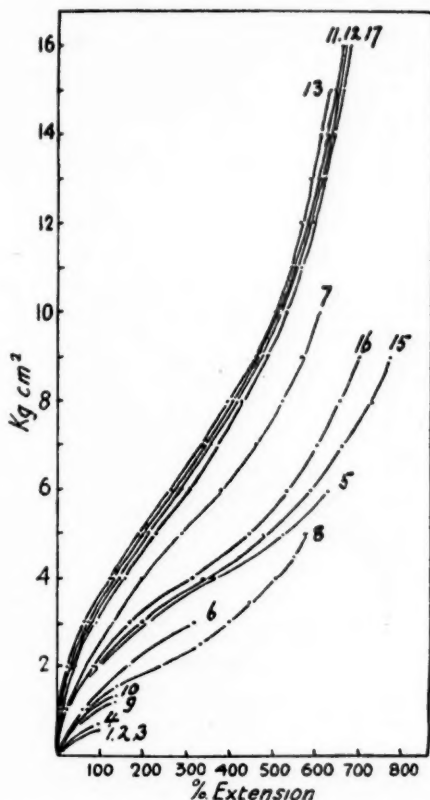


Fig. 10.—Insolation of milled rubber in air, the under-surfaces dusted with sulfur, sulfur and accelerators and accelerators alone. For significance of numbering, see Table II (5).

terized, as in thermal cases by brittleness or shortness, a dry appearance and a large acetone extract—up to 12 per cent has been found. When correctly photovulcanized, specimens yield 3 to 4 per cent, as in thermally vulcanized rubbers. Also a photoovercure becomes increasingly apparent with length of storage in the dark, as in the case of thermal vulcanizates. No overcure has so far been obtained in the absence of oxygen. The optimum exposure probably varies with each sensitizer (photovulcanizing agent). The lie of the curves is not quite in the same order as with the vacuum-insolated, but as a whole the results indicate a similar efficiency for individual sensitizers.

In some instances there is a difference in the slope of the curves. Those giving the maximum tensiles seem to flow parallel to one another and spread out fanwise in the usual manner. But some reagents, as for instance chlorobenzanthrone, phenanthrenequinone, thiocarbanilide and alizarin (see Figures 7, 8, 9 and 10) give more S-shaped curves or curves with a pronounced bulge. The differences in slope appear to be too great to be accounted for as experimental errors and may be attributed to irregular penetration of vulcanization, as these curves more resemble those shown by cold cures (Figures 4 and 5).

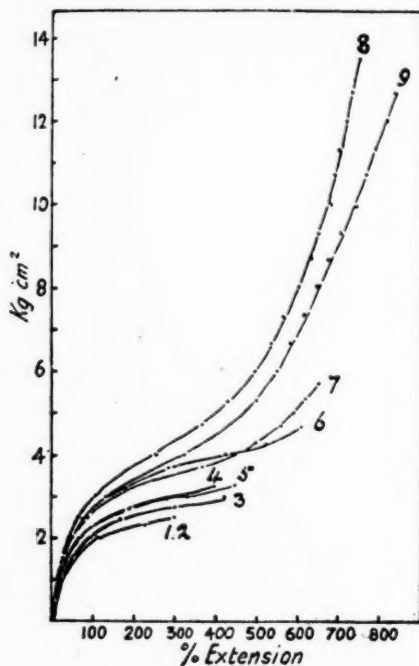


FIG. 11.—Irradiation with ultraviolet light and sensitizers in air for 12 and 24 hours. For significance of numbering, see Table IV.

#### VULCANIZATION ACCELERATORS BOTH IN PRESENCE AND ABSENCE OF SULFUR

Thermal-vulcanization accelerators in the absence of sulfur are much less effective sensitizers or agents than aldehydes, ketones or quinones, and resemble in activity substances like aurin and alizarin (Figure 9). Mercaptobenzothiazole exerts protective action and often gives a good result even in the presence of air, as also do the diethyldithiocarbamates to a lesser extent. A number of experiments have been made with combinations of sulfur and accelerators, both alone and in the presence of stearic acid, with and without zinc oxide. Sometimes small variations were shown in either direction and are attributed to experimental error. The specimens for which the results are given in Figure 10 show practically identical curves, all being coated with reagent on the under-surface only. It is concluded that thermal-vulcanization accelerators have no photochemical accelerator action.

TABLE III  
PROPERTIES OF PHOTOVULCANIZATES OBTAINED BY INSOLATION

Sensitizer	Load at 600% extension (kg. per sq. cm.)	Swelling index	Proportion soluble	Combined sulfur (percentage)
(1) INSOLATION IN ISOBUTANE FOR FOUR MONTHS. CORRESPONDS TO FIGURE 6				
0. None	4.0	15.8	0.15	—
1. Alizarin	3.6	54.2	0.50	—
2. Benzoquinone	5.1	63.2	0.60	—
3. Sulfur	8.0	32.8	0.27	0.38
4. Chloranil	15.5	46.7	0.33	—
(2) INSOLATION IN VACUO FOR FOUR MONTHS. CORRESPONDS TO FIGURE 7				
1. Selenium	* 1.0	—	Wholly soluble	—
2. Benzoquinone	* 1.5	101.2	0.63	—
3. Eosin	* 2.8	52.0	0.65	—
4. <i>p</i> -Phenylenediamine	* 2.8	—	Wholly soluble	—
5. Hydroquinone	* 2.8	86.5	0.56	—
6. Diphenylguanidine	* 2.8	—	Wholly soluble	—
7. Benzidine	* 2.8	40.5	0.62	—
8. Sodium diethyldithiocarbamate	3.7	82.6	0.57	0.22
9. Zinc diethyldithiocarbamate	4.3	91.0	0.56	0.23
10. Chlorobenzanthrone	* 8.0	23.6	0.26	—
11. Benzophenone	10.2	19.4	0.33	—
12. Xanthone	11.0	10.9	0.10	—
13. Sulfur	12.0	44.0	0.28	0.65
14. Chloranil	14.1	29.8	0.31	—
15. Dichloroanthroquinone	18.5	18.8	0.18	—
16. Anthraquinone	†26.0	12.2	0.14	—
* Maximum figures at any extension. † By interpolation.				
(3) INSOLATION IN AIR FOR THREE SUNNY DAYS. CORRESPONDS TO FIGURE 8				
0. None	1.0	—	Soluble	—
1. Selenium	1.6	—	Mainly soluble	—
2. Eosin	1.6	—	" "	—
3. <i>p</i> -Phenylenediamine	1.6	—	" "	—
4. Benzidine	3.0	—	0.62	—
5. Zinc diethyldithiocarbamate	4.3	91.0	0.56	—
6. Phenanthrenequinone	4.3	39.5	0.39	—
7. Chlorobenzanthrone	5.9	23.6	0.26	—
8. Sulfur	9.8	21.2	0.25	0.36
9. Anthraquinone	11.0	12.2	0.14	—
10. Chloranil	11.8	29.8	0.31	—
11. Xanthone	14.6	8.9	0.09	—
(4) INSOLATION IN ISOBUTANE. CORRESPONDS TO FIGURE 9				
1. MA	3.1	60.3	0.45	—
2. Mercaptobenzothiazole	3.2	42.0	0.34	0.31
3. Selenium	3.4	—	—	—
4. Alizarin	4.0	38.1	0.38	—
5. Diphenylguanidine	3.7	52.8	0.47	—
6. Aurin	4.4	32.7	0.29	—
7. Sulfur + diphenylguanidine	6.2	29.3	0.29	0.57
8. Sulfur + MA	6.7	29.3	0.27	0.60
9. Sulfur + mercaptobenzothiazole	8.0	16.9	0.13	0.79
10. Sulfur (upper surface coated)	7.8	20.4	0.19	0.54
11. Sulfur (under surface coated)	8.2	21.1	0.21	0.68
12. Sulfur (both surfaces coated)	8.0	19.6	0.19	0.64
(5) INSOLATION IN AIR. CORRESPONDS TO FIGURE 10				
1-3. DPG, RN and PT	2.0	—	Mainly soluble	—
4. MA	2.0	60.3	0.45	—
5. Zinc diethyldithiocarbamate	* 5.7	23.0	0.22	0.18
6. Mercaptobenzothiazole (both surfaces coated)	3.1	15.5	0.24	0.37
7. Mercaptobenzothiazole (under surface only coated)	9.8	10.6	0.19	0.23
8. Thiocarbamilide	5.6	25.1	0.31	0.10
9. Alizarin	2.0	60.7	0.54	—
10. Aurin	2.0	58.0	0.55	—
11. Sulfur + diphenylguanidine	12.5	11.1	0.15	0.95
12. Sulfur + hexamethylenetetramine	12.7	11.1	0.17	0.89
13. Sulfur + mercaptobenzothiazole	13.3	11.1	0.15	0.92
14. Sulfur + thiocarbamide	11.4	11.0	0.08	0.76
15. Sulfur (both sides coated)	6.2	12.1	0.17	0.80
16. Sulfur (upper side only)	7.0	10.5	0.17	0.59
17. Sulfur (under side only)	12.6	11.2	0.17	1.12

All photovulcanizates 11-17 became short and brittle on aging at normal temperatures in the dark for nine months and, in consequence, give at least double the figures for proportion soluble. This applies particularly to 17, which was more overcured than the others. The figures for swelling index are not affected.

DPG = diphenylguanidine.

RN = polymerization product of ethyldene-aniline.

PT = aldehydeamine type of accelerator similar to RN.

MA = condensation product of formaldehyde and aniline.

Table III (4) gives the results of a number of swelling tests, solubility tests and where applicable, percentages of combined sulfur in a series insolated in inert gas (Figure 9). The addition of accelerators to the sulfur has made no appreciable difference in the combined sulfur figures. The accelerators by themselves give poor results but have played a part in the reaction as the sulfur-containing accelerator mercaptobenzothiazole has suffered photolysis, and an appreciable amount of sulfur has combined with the rubber. In physical properties this specimen closely resembles those obtained with the less active accelerators M.A. (condensation product of formaldehyde and aniline) and diphenylguanidine. In contrast, in the presence of air (Figure 10) these latter caused marked softening and no tensile figures could be obtained. The same applies to R.N. (polymerized ethyldeneaniline) and P.T. (aldehydeamine-type accelerator). All these are soluble accelerators, and readily dispersed in rubber.

#### IRRADIATION OF DRY RUBBER IN ULTRAVIOLET LIGHT

Rubber was also irradiated in ultraviolet light under similar conditions. This was relatively slow in action. Exposure of the rubber without added reagents 15 cm. from a lamp (4 amps., 40 volt) for 1-5 hours produced no appreciable effect in exhausted tubes, whether of glass or silica. The irradiated specimens were readily benzene-soluble in the dark. Under the same conditions, but with reagent rubbed on to the surface and in the presence of air, a perceptible effect was obtained in five hours, particularly with chloranil, which gave a load of 4.4 kg. at 600 per cent extension, and with sulfur, which gave a load of 3.8 kg. With longer periods, *e.g.*, 12 and 24 hours, higher figures were reached. Some curves for these are given in Figure 11 and data in Table IV.

TABLE IV  
PROPERTIES OF VULCANIZATES OBTAINED BY ULTRAVIOLET IRRADIATION.  
CORRESPONDS TO FIGURE 11

Sensitizer	Period of exposure	Load at 600% extension (kg. per sq. cm.)	Swelling index	Proportion soluble	Combined sulfur (percentage)
1. Mercaptobenzothiazole	12 hours	*3.8	56	0.93	0.19
2. Zinc diethyldithiocarbamate	12 "	*2.8	66	0.73	0.18
3. Tetraethylthiuram disulfide	12 "	*4.0	108	0.80	0.25
4. Benzoquinone	12 "	*4.6	93	0.72	—
5. Benzoquinone	24 "	4.7	85	0.79	—
6. Sulfur	12 "	4.7	63	0.78	0.14
7. Sulfur	24 "	5.0	96	0.76	0.20
8. Chloranil	12 "	8.1	36	0.31	—
9. Chloranil	24 "	7.1	64	0.50	—

\* By extrapolation.

If they are compared with parallel experiments in which the same rubber was insolated for three sunny days, Figure 8, it will be seen that this period of exposure to sunlight is more effective than 24 hours' irradiation with the ultraviolet lamp. Further, the latter reaches a maximum effect in air in 12 hours, there is little improvement after a further 12 hours' irradiation, often the reverse. This indicates that the ultraviolet rays bring about a greater photolysis or photooxidation than sunlight, and that the vulcanizing agent is less able to protect the rubber from physical deterioration. Little is known regarding the spectral sensitivity of rubber. It is not intended to explore the subject here but the following observations are recorded. The work of Pummerer and

Kehlen<sup>8</sup> indicated that relatively short wave lengths—not in excess of 3150—are effective for photogelation, a similar sensitivity would be anticipated for dry rubber. This is unexpected having regard to the ready penetration of the glass walls of the containers by the photovulcanizing rays, and the greater vulcanizing effect of sunlight as compared with ultraviolet lamp irradiation. Indeed it may be that the visible rays emitted by the lamp are the effective ones and that the shorter waves tend to have the reverse effect, that is a photolytic or oxidative action. There is also no relation between ultraviolet light and sunlight in regard to accelerated light ageing tests<sup>9</sup>. Much of the active radiation which penetrates the rubber passes through without being absorbed. In one experiment the pieces of sheet rubber in exhausted tubes in sunlight were backed with pieces of filter paper dyed black. These were gradually bleached. The bleaching was most pronounced in the tubes containing sulfur and sulfur mixtures and much less in the tubes with accelerators alone or such relatively inefficient agents as aurin and alizarin. Selenium powder was opaque, and with this exception there was no relationship between transparency to visible light and the passage of the rays which caused bleaching of the dyed paper beneath.

#### OTHER PHOTOVULCANIZATION PROCESSES

Photovulcanization may also be obtained by insolation of rubber immersed in solutions of reagents in nonrubber solvents such as water and acetone, but the products so far obtained are physically inferior to those obtained in air or vacuo. A number of experiments were made with an aqueous solution of benzoquinone. The strips of rubber were placed flat at the bottom of Petri dishes and the solution was frequently renewed. A maximum tensile of 5 to 6 kg. per sq. cm. was soon attained, but further insolation caused gradual reduction in tensile and modulus. In no case was the vulcanization far enough advanced to prevent "freezing" of the specimens stored over the winter including those which were short and apparently overcured. A simple method for the preparation of large sheets of photovulcanized rubber is to lay the sheet flat between two layers of cellophane and seal the edges hermetically with cellulose lacquer. Any oxygen entrapped is soon absorbed so that the effect obtained is more that of insolation in vacuo.

It is of course, practicable to photovulcanize unmilled raw rubber either as a latex film or in crepe or sheet form in the manner described, but these types have not been used for the quantitative work for the reasons already given.

It is of interest to recall that the indigenous Brazilians use powdered sulfur for counteracting the tackiness of crude latex treated cloth in the manufacture of ponchos, and N. Hayward in 1861 used sulfur in a similar manner. The writer examined a sample of poncho cloth some years ago. It behaved as if vulcanized, the rubber contained a total of 1.57 per cent of sulfur of which 0.91 per cent was combined. The author in the course of his remarks suggested that "it was possible that the vulcanization was brought about by exposure to the sun"<sup>10</sup>, but at that time the implications were not realized.

There is nothing in the feel or appearance of insulated or irradiated rubber to indicate that it has not been thermally vulcanized. With sulfur as agent, the rubber darkens during vulcanization, even in the absence of air, as it does thermally. Substances with pronounced color impart their color to the rubber. In the absence of a sensitizer, the natural light yellow color of the rubber is bleached, but the red color imparted by aurin is not bleached. The vulcanizates

exhibit the usual indifference to temperature changes when sufficiently vulcanized, and remain pliable and transparent at winter temperatures. They also swell less in solvents and less is dissolved. Some figures for modulus are given in the Tables with the corresponding figure for swelling index and the proportion soluble in benzene to correspond with the curves. There is no very close relationship between the modulus and other properties, although they show some concomitant variation. A plot shows several appreciable deviations from the average. The photovulcanizates obtained without any sensitizer lie at intermediate positions and exhibit a similar relationship between the tensile and swelling properties, as do the sensitized specimens. It is mainly a matter of degree and rate of cure, although some physical differences are noticeable according to the reagents used. Thus, chloranil seems to harden the surface, which may develop crazing after long exposure in air while the under-surface is still supple and elastic. Sulfur has not this surface hardening effect.

#### EXPERIMENTAL

The vulcanized rubber used (Figures 1 and 2 and Table II) consisted of 93 per cent pale crepe, 1.85 per cent sulfur, 1 per cent zinc oxide and magnesium carbonate, with a small quantity of stearic acid and plasticizers. The accelerator consisted of 0.5 per cent each diphenylguanidine and mercapto-benzothiazole.

The raw rubber used for exposures consisted of milled sheeted crepe or cut sheet of thickness, usually 1 mm. The latter type of rubber is preferable because it shows no calender grain although none was found in the calendered sheet employed. The reagents used were as purchased, the sulfur being the ordinary flowers of sulfur. The surface of the rubber was wiped with a benzene-saturated rag, and allowed to dry off before dusting with powdered reagent, which was well rubbed into the surface with the ball of the finger or a small piece of rag. The amount of sulfur so retained by a rubber sheet 1 mm. thick, coated on one side was about 2-3 per cent, thus providing ample margin for vulcanizates, all of which contained appreciably less than 1 per cent combined sulfur.

For working in vacuo or inert gas strips were attached to a strip of thin glass by binding once with cotton. The thicker sheets required no binding. For small experiments 0.75 inch diameter x 6 inch test-tubes with a 0.5 mm. thick wall are suitable. These are drawn out after inserting the rubber. A few drops of petroleum ether were introduced through a capillary funnel before exhausting. The better vacuum thus obtained was without noticeable effect. For larger samples the tubing had a 1 mm. thick wall. The isobutane gas was bubbled through alkaline pyrogallate. For insolation the tubes were set in rows at a slant, on shelves fixed to a wall with a southwest aspect.

The solvent-swelling test was carried out by immersing about 0.1 g. in 10 cc. of benzene in corked tared test-tubes in the dark for three days when the benzene was decanted, replaced, and the tube set aside in the dark for a further seven days, after which the benzene was poured off as completely as possible and the sides of the tube and surface of the gel (where firm enough) were dried with a plug of cotton wool on a wire large enough to fill the tube. After weighing the gel, the benzene was removed slowly by exposure to the air and completed in a water oven till constant. The swelling index being the volume of solvent taken up per unit volume of rubber, is calculated on the insoluble part, not on the weight of rubber taken. Combined sulfur was estimated directly

on the acetone-extracted rubber. It was found necessary to extract at intervals over three days in the dark, to be certain of removing all the uncombined sulfur.

The tensile test-piece 1 cm. wide and 3 cm. long was cut with scissors from a sheet. Fine lines 2 cm. apart were ruled in ink, and the strips were held by plain screw clips just above and below the marks. A light aluminum pan weighing approximately 50 grams was attached to the lower clip and the rubber stretched by adding 50 grams or in some instances 100 grams at a time. Rate of addition of load (except where this was intentionally varied—Figures 3 and 5) approximated to 1.5 kg. per minute, calculated for a strip 1 sq. cm. cross-section. After each addition the distance between the marks was read. Weak specimens often tear in several places at the edges, giving a frilled edge and break at some point between the grips. The graphs do not record the maximum tensiles. This, however, is of less importance than the shape and position of the curves, and by using straight test-pieces, various complications are avoided. In a few cases when more representative figures for maximum breaking load were required, dumb-bell shaped specimens were cut giving a waist width of 0.3 mm. and end width 2 cm., the length being 2 cm. as before. Where sheets are exposed to sunlight it is important to keep them from crumbling or bellowing as this leads to irregular exposure, and some parts of the sheets are more cured than other parts. For this reason it is not satisfactory to expose sheets of less than 1 mm. thick of an area greater than 1 or 2 sq. inches. To keep thin sheets flat, they should be fixed to glass plates.

#### SWELLING SOLUBILITY AND COMBINED SULFUR RELATIONSHIPS FOR THERMAL VULCANIZATES

Incidentally the graphs Figures 2 and 3 and Table II throw some light on the minimum proportion of combined sulfur required to confer on rubber the properties of a vulcanizate, that is to say in the light of present concepts, the minimum of sulfur which combines during the formation of sufficient cross-links for the development of the properties of a vulcanizate. The question has been previously debated<sup>11</sup>, and the figure has been put as low as 0.15 or 0.10 per cent. It has been assumed that there exists a sharp conversion point, whereas it is more probable that there is no definite stage in the vulcanization at which the change to vulcanized rubber appears. A survey shows that the stress-strain relationship is the most sensitive to vulcanization. A very small initial change makes itself apparent in the slope and position of the curve. Swelling and solubility figures are also sensitive, but data are unreliable or even lacking at the initial stages because the rubber swells so considerably and the gel is so weak that the solvent cannot be completely separated and removed. A very slightly vulcanized rubber is substantially soluble in benzene. More definite figures are obtained in such cases by using petroleum ether in the place of benzene. The freezing test is the least sensitive of any. Thus 4 of Figure 2 with combined sulfur of 0.22 per cent may be said to show a definite degree of vulcanization. When stretched it does not exhibit a yield-point like 1, 2 and 3, yet on exposure to 0° it hardens similarly to the raw mix. When using an ultra-accelerator, 0.5 per cent of combined sulfur corresponds to a substantially fully cured rubber.

#### RELATIONSHIPS FOR PHOTOVULCANIZATES

The figures from photovulcanized specimens Figures 6-9 are of the same order, and vary with the conditions of exposure. In vacuo, without sensitizer,

the figures so far obtained are not much inferior to those obtained with sulfur; thus for 5, Figure 1, the lie of the curve is not far removed from that of a sulfur-sensitized rubber; for instance 3, Figure 6. This latter contains 0.38 per cent combined sulfur. It should be noted that the corresponding figures for swelling and solubility are relatively lower for the photovulcanizate exposed without a sensitizer. 5, Figure 1, also lies between the two curves 5, Figure 2, indicating that the degree of vulcanization attained without sensitizer is equivalent to a thermally vulcanized rubber with 0.25 to 0.37 per cent combined sulfur. It may, therefore, be said that the degree of physical vulcanization shown by a piece of rubber insulated by itself in vacuo for a year is equivalent to that which could be obtained with a combined sulfur of about 0.3 per cent. By contrast, ultraviolet-irradiated rubber, sulfur-treated, gave only 0.2 per cent or less, with correspondingly high swelling and solubility figures.

The results obtained with benzoquinone are generally poor. Analogously, benzoquinone is not a photogelling agent, although thermally it was found to be more efficient than other quinones. The efficiency is similarly reversed with respect of sulfur, which is a better thermal vulcanizing agent than the chlorinated quinones, while photochemically the reverse is the case. If the mode of action of an accelerator of thermal vulcanization were understood, it might be possible to explain the above noted relationships, which may be summed up, as follows:

- (1) Photovulcanization can be obtained by exposure to light without any sensitizer or other agent, and the degree of vulcanization produced after one year's exposure in a glass tube in the absence of air corresponds to that of an accelerated sulfur mix with about 0.3 per cent sulfur combined.
- (2) Accelerators for thermal vulcanization do not promote photovulcanization with sulfur.
- (3) Many accelerators act as photovulcanization promoters by themselves without elemental sulfur, although weakly.
- (4) Sulfur is a much better thermal vulcanizing agent than some quinones and chlorinated quinones, but the latter are more efficient photovulcanizing agents.

#### DISCUSSION ON VULCANIZATION RELATIONSHIPS

A theory adequate to account for the mechanism of photovulcanization would carry with it the key to the problem of thermal vulcanization, for the products are indistinguishable, and in many cases the same reagents may be used. We cannot therefore expect a complete explanation of the results here recorded but, taken in conjunction with our knowledge of thermal vulcanization, it is possible to put forward a view of the mechanism of the process.

The ineffectiveness of thermal vulcanization accelerators for photovulcanization is readily accounted for when it is remembered that these accelerators are not active thermally at the maximum temperatures encountered on exposure to sunlight. This seldom exceeds 50° and never reached 60°, the temperature being recorded on a thermometer with the bulb wrapped in a thin sheet of the rubber. On this account it was obviously useless to try such ultra-accelerators in conjunction with sulfur as are active below 60° C, as the thermal effect would have been indistinguishable from the photo-effect.

The data available on photovulcanization can serve as a check on the theories advanced from time to time in explanation of thermal vulcanization. For the latter, the current theory as is well known, postulates a cross-linking

of the long hydrocarbon molecules by primary valences, either directly or more generally through an intermediate element, either sulfur or oxygen. In the latter cases the amount of combined sulfur or oxygen in the system should be a measure of the number of cross-linkages and consequently also of the degree of vulcanization. As, however, there is only proportionality between sulfur content and physical properties when the method of vulcanizing and the reagents taking part are the same, it must follow that sulfur in vulcanized rubber cannot function only as a member of a cross-linkage. It seems rather that binding of sulfur in ordinary thermal vulcanization is a reaction which probably goes on independently of cross-linking, assuming that the latter really is the direct cause of those changes which are characteristic of vulcanization. These, shortly, are (1) improvement in physical properties, (2) increased resistance to solvent action and (3) indifference to a wider range of temperatures. The fact that rubber can be thermally vulcanized without sulfur, as *e.g.*, by means of dibenzoyl peroxide, necessitates the assumption that oxygen can take the place of sulfur in the link. Hence it is of considerable importance to ascertain if the characteristics of a vulcanizate as epitomized above, in however small a degree, are obtainable without either of these agents. As photovulcanization involves insolubilization of the rubber, it would appear probable that the photogelation of a raw rubber sol is caused by the insolubilization of the rubber in solution, which then separates as a gel exactly in the same way as happens when a rubber sol is heated with sulfur and accelerator, or when small quantities of sulfur chloride or dithiocyanogen are added in the cold. It has been shown that rubber sols without the addition of any vulcanizing agent, gel slowly when insolated in inert solvents, and every attempt to prevent the reaction by most careful exclusion of oxygen has failed<sup>12</sup>. Similarly rubber is photovulcanized in vacuo without addition of any agent or sensitizer.

#### THE FUNCTION OF AGENTS OR CATALYSTS

Although substantial quantities of oxygen delay gelling and prevent photovulcanization, and mere traces seem to be without effect, the author has recently observed that small quantities from 0.01 to 0.5 per cent on the rubber expedite the change. All the evidence indicates that neither sulfur nor oxygen need play a part in vulcanization except as catalysts, in which case, if the cross-bonding theory be accepted, vulcanization in certain cases may be the result of direct primary linkages connecting individual long-chain molecules. Although rubber insolated in vacuo without any vulcanizing agent acquires the properties of vulcanized rubber, the possible agency of oxygen cannot be excluded as it is not practicable to remove the oxygen dissolved in the rubber. The amount of such oxygen must be very small and insufficient to account for a marked degree of cross-bonding, particularly having regard to the well-milled condition of the rubber. On the other hand there would be ample oxygen to initiate a chain reaction.

It is common knowledge that the optimum physical properties obtainable with variously vulcanized rubber differ very considerably. Thus with the thermally vulcanized, the tensile properties are considerably enhanced by the use of an accelerator, and the more efficient the accelerator the greater the improvement. Or again, other vulcanizing agents give variable and inferior products. The same is noted in the case of photovulcanized rubber, and it is clear that concurrently with the true vulcanizing action, as measured by physical change, there proceeds chemical reactions which may be both additive and

substitutive, and which do not contribute to the enhancement of the physical properties but rather the reverse. The various catalysts or sensitizers which promote photovulcanization also react chemically with the rubber to form by-products which have not high elasticity. If this be accepted, a variety of rubber derivatives will be obtained, as in photogelation, which do not contribute to the elasticity of the vulcanizate. A measure of the sulfur, chlorine or other element which has entered into combination with the rubber is therefore in part a measure of this side-reaction, and may be no measure of vulcanization. It is desirable, therefore, to keep these side reactions in abeyance as far as possible, and the most efficient vulcanizing agent, thermal or photochemical, will be the substance or combination of substances which are the most effective catalysts and the least chemically reactive to the rubber. In those cases in which vulcanizing agents are not used, either some substance natural to the rubber and present in it functions as a catalyst or the photoreaction can proceed without a catalyst, in this respect differing from the thermal process. As purification of rubber has not much effect on the rate of photogelation or in some cases accelerates it, similarly purification should not retard photovulcanization, therefore naturally occurring catalysts for photoreactions may be taken to be absent from raw rubber. It seems more likely that excitation of the long molecules of the rubber or more probably of short sections of the same, by light of appropriate wave lengths, is sufficient to enable adjacent portions of these chains to link up in places and thus, in accordance with the modern viewpoint confer the property of high elasticity on the rubber, although the tensile properties thus produced are poor compared with a thermally vulcanized rubber activated with sulfur and fully cured.

#### POSSIBLE COLLOIDAL ORIGIN OF HIGH ELASTICITY

Judged by the essential similarity of the curves given by the thermal and photochemically vulcanized rubbers and the low figures for modulus and tensile, the thermal and photochemical effects may be taken to be identical at low degrees of vulcanization such as the 5- and 10-minute cures (Figure 2). The difference then between thermal and photochemical vulcanization lies in the capacity of the former to be carried to a degree of physical vulcanization considerably out-stripping the maximum so far obtained photochemically, *i.e.*, up to a ten-fold increase of modulus and tensile. It seems that at the early stages, high elasticity in a pronounced degree is obtained with very low modulus, and that further vulcanization increases the modulus without much increase in limit of extension and recovery therefrom. The behavior of well milled rubber when initially vulcanized closely resembles that of a strip of putty, and possibly justifies a return to an older outlook, namely, that a great part, if not all, of the elastic properties of rubber and rubberlike materials may be attributed to a coarser structure than that of individual molecules.

Alternatively the initial effect of vulcanization (cross-bonding) is to anchor some of the rubber chains, so that instead of slipping past one another when a tension is applied, as in the plastic milled state, sufficient of them are linked up to restrain the slip and cause the molecule to uncurl and straighten out. According to Treloar<sup>13</sup> a theoretical treatment indicates a possible maximum extension of 2.5 to 4 times the experimental figure for raw rubber. How far this applies to the relatively short and presumably oxidized molecules of milled rubber is not clear. If in unmilled rubber the molecules are interlocked at a few places to form a 3-dimensional network, such interlocking must be destroyed

by plasticization, or the milled rubber would not be predominantly plastic. Initial vulcanization would introduce a few cross-links which would take the place of the interlocking postulated for unmilled raw rubber. But this new cross-linking resulting from initial vulcanization must be of a different nature or configuration from that presumed to be present in unmilled raw rubber, as it confers insolubility, greater tolerance to temperature changes, and eventually much improved physical properties which are absent from raw rubber.

In this connection it has already been noted above, that stiffening of the mass and some return to elastic properties appear in rubber initially vulcanized, before insolubility and indifference to temperature changes are noted. This might be interpreted as favoring the identical type of interlocking for raw and vulcanized rubber; but if a comparison be made between, say sole crepe, for which figures of about 50 kg. cm<sup>-2</sup> and an extension at break of 700–800 per cent have been recorded<sup>14</sup>, and a milled rubber vulcanized to give similar figures, the latter would be substantially insoluble in all solvents and resistant to “freezing”.

### SUMMARY

Milled sheeted rubber in evacuated sealed tubes or tubes filled with inert gas becomes vulcanized on exposure to sunlight or ultraviolet radiation. Stress-strain curves and also swelling and solubility data are given in confirmation. The vulcanizing effect is enhanced by treating the surface, preferably the under-surface, of the rubber with sensitizers, which may be regarded as photovulcanizing agents. These usually are also photogelling agents, and comprise aldehydes, ketones, quinones and chlorinated quinones. Sulfur is also active, and to a lesser extent other substances, including some thermal-vulcanization accelerators, although these latter do not act as photovulcanization accelerators. Some photovulcanizing agents protect rubber from oxidation during insolation, so with them a vulcanizing effect is obtainable in the presence of air. The nature of the photovulcanizing effect and its relation to modern theories of vulcanization are discussed.

### ACKNOWLEDGMENT

I am indebted to Professor R. W. G. Norrish and R. R. Smith for exposing specimens to ultraviolet; to H. Rogers and G. Martin, and the R.A.B.R.M., and also E. H. Lenten of J. G. Franklin and Sons, Ltd., and other manufacturers for supplies of raw materials.

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## MOLECULAR REQUIREMENTS FOR SYNTHETIC RUBBERS \*

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Rubbery substances consist basically of long chains of atoms to which other atoms may be attached in small groups that occur repeatedly, and often regularly, like the links along a chain. There are hundreds of atoms in one of these "macro" molecules. It is the particular arrangement and the active forces between these molecules that are responsible for the elastic properties of many substances. The structure of the molecules of most synthetic rubbers as well as that of natural rubber is so complex, however, that efforts to determine, by direct study of the commercial products, what produces their rubbery characteristics have yielded results that are difficult to interpret. Progress in solving the puzzle has recently been made by starting with simple chain compounds and forming from them, by known chemical modifications, substances which have some of the properties that are found in natural rubber.

Studies of these "model" chain compounds indicate that the long-chain molecules of rubbery substances must have forces between atomic groups which are small enough to permit twisting and kinking of the chains. There must also be lateral forces to hold adjacent molecules together, like a bundle of sticks, especially when the substance is stretched. Moreover, the molecules must have side groups to avoid the close packing, when unstretched, that is characteristic of crystals.

The simplest carbon-chain molecules are those of the paraffin group, of which polyethylene is an example. Its structure is shown schematically in Figure 1. This polymer is somewhat elastic at high temperatures, but it then lacks tensile strength, which indicates weak lateral attractive forces between molecules. At ordinary temperatures, these chain molecules also form semi-crystalline solids which are rather inflexible.

Intrachain stiffness can be overcome in these substances by introducing oxygen or other atoms between some of the carbon atoms. This also produces unneutralized lateral forces, which tend to attract adjacent molecules, a tendency that likewise results from adding certain side groups, such as phenyl, to the molecules. To prevent this attraction from progressing to the extent of causing crystallization in the unstretched condition, other side groups such as methyl, are introduced at regular intervals along the chain, as is illustrated schematically in Figure 2 for polypropylene sebacate.

The Laboratories' studies of these polyesters indicate that the characteristic of many rubbery substances which gives them tenacity is the formation of atomic groups in which some of the positive and negative charges have been separated, thereby giving the group dipole properties. These separated charges attract their opposites in the dipoles of molecules on both sides of them, and provide the strength and toughness required in synthetic rubber. This

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head-to-tail arrangement of the dipole groups orients them in layers which are illustrated in Figure 2 by the sloping lines. X-ray diffraction studies and measurements of the modulus of elasticity have confirmed this dipole layer formation in many model rubber compounds. If the dipole forces are too strong, however, crystalline solids result. This condition can be modified, as stated above, by introduction of methyl side groups at or near the polar layers. Similar results are obtained by placing methyl groups actually within the polar layers of the model rubber compounds.

When natural rubber is stretched, its tensile strength becomes greater, because crystals are formed, with consequent closer packing of atomic groups and increase of intermolecular forces. The same is true of polyester "model molecules" used in these studies. Figure 3A shows an x-ray diffraction pattern

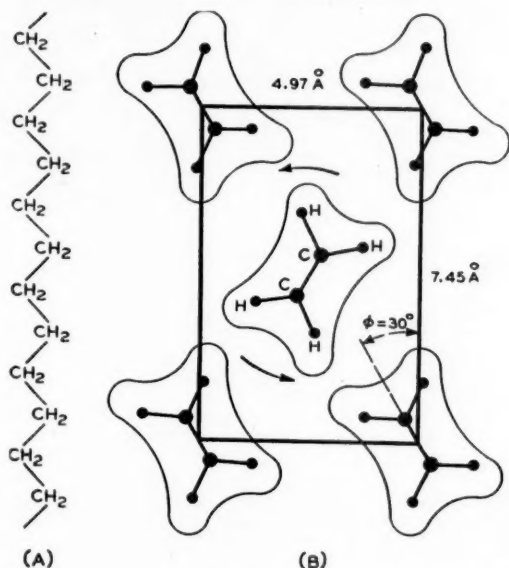


FIG. 1.—Rubbery substances consist of long chains of carbon atoms to which other atoms are attached as side groups, replacing hydrogens. These chains, without the side groups, are illustrated by the structural formula of the polyethylene molecule. At the right are shown cross-sections of these chains. The enclosed areas represent electrical fields around them.

of polypropylene sebacate from a specimen which was elongated sixfold at 25 degrees C after the gum had been vulcanized to keep it from creeping, since this polymer is fluid at slightly above room temperature.

Polyester models show the properties of a true rubber by the complete disappearance of crystallization on relaxation. Figure 3B was made from a relaxed specimen which had been repeatedly stretched. The pattern is typical of amorphous scattering. In contrast to natural rubber, however, crystallinity does not develop immediately on stretching these polyesters. This is illustrated by comparing the relatively disordered pattern of Figure 3C, where the specimen was stretched and photographed at once, with the comparatively rich crystallinity of Figure 3A, in which case it remained stretched twenty-four hours before exposure. Delay of orientation on stretching limits the "instantaneous" tensile strength of the compounds, and is accompanied by internal

friction with consequent hysteresis loss. Nevertheless, the gum stocks of these model polymers exhibit high elasticity and quick recovery from deformation.

When methyl side groups are added to chain molecules to prevent the polymers from crystallizing at room temperature, they may be inserted in

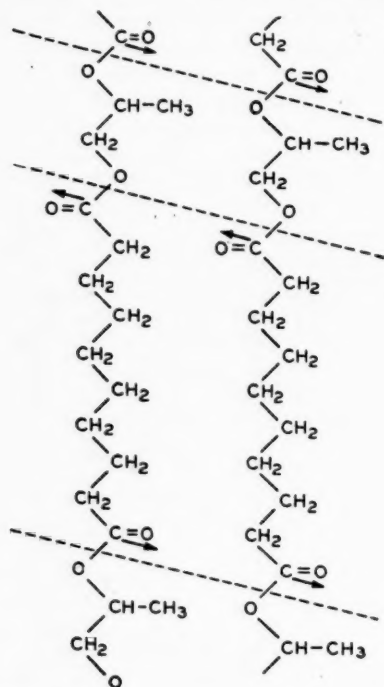


FIG. 2. The broken lines across this structural formula of polypropylene sebacate show the layers within which there are attractive forces caused by separated positive and negative electrical charges. These attractive forces provide the strength and toughness that is required of rubber.



FIG. 3. x-Ray diffraction patterns of polypropylene sebacate. Pattern A shows marked crystallinity. It was made after the specimen had remained stretched twenty-four hours. Pattern B was unstretched and is amorphous. Pattern C shows little crystallinity because it was photographed immediately after stretching.

different parts of the molecule and their effect on the atomic spacings depends on their location. If the methyl groups are introduced next to the ester group of a dipole layer, Figure 2A, x-ray diffraction studies show that the molecular chains spread and increase the lateral spacing by a few per cent.

Another result of introducing methyl groups is an effect like random rotation of sections of the molecules about their long axes. This causes disorder, which can be detected by diffraction patterns. Thus Figure 4A, obtained from polyethylene sebacate before introducing methyl groups, shows two sharp and intense outer rings. Only one can be seen in Figure 4B, which was made from this polymer after substituting methyl groups in it. This indicates that the particular orientation around the long-chain axes, which is responsible for the other ring, shown in Figure 4A, has deteriorated.

Since the forces between chain molecules drop off at least as the third power of the mean separation of attraction centers, small changes of spacing may

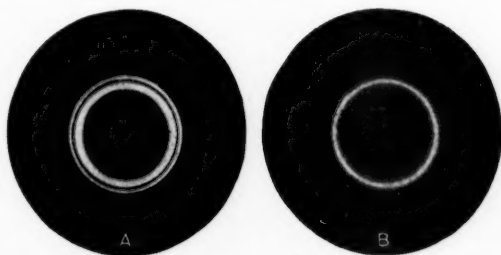


FIG. 4.—Adding methyl groups to polyethylene sebacate causes an effect like random rotation of the molecules about their long axes. This has made the outer ring of A disappear in B, which was taken after methyl radicals had been added.

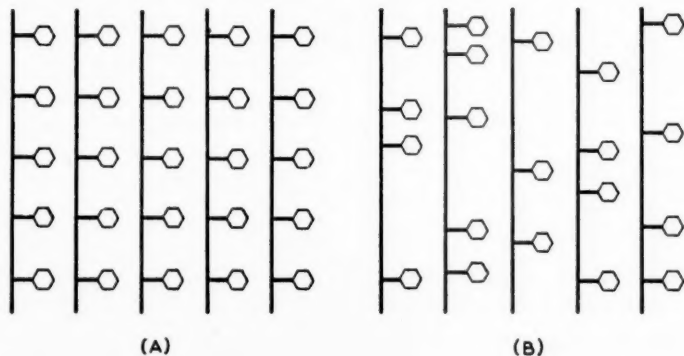


FIG. 5.—In natural rubber and in an ideal synthetic rubber the points of attraction of adjacent chain molecules come opposite each other when the specimen is stretched, as is indicated at A. Actually in GR-S rubber the phenyl groups, which provide these points of attraction, are irregularly aligned, as shown at B, and thus the product is weakened.

make a large difference in the stiffness of the material. The disordering noted above is accompanied by such an increase in spacing, and this may convert a hard plastic into a rubbery material.

Application of these principles to the GR-S synthetic rubber which is now being made in large quantities in this country is illustrated by the schematic diagrams of Figure 5. An ideal GR-S, Figure 5A, would have a structure analogous to the polyester models, and the attraction forces between parallel molecules would be supplied by the phenyl groups. On stretching, these groups would form layers. Actually the condition in GR-S is probably more nearly

represented by Figure 5B. The styrene residues, with their phenyl groups, occur irregularly along the molecular chains. Therefore, when the chains are roughly aligned by stretching, the phenyl groups in adjacent chains do not all come opposite each other. Thus, at many points high attractive forces remain uncoordinated, and help little in tying the gum together. This deficiency can be lessened by more complete polymerization of the gum, which increases the probability of some of the phenyl groups of any two adjacent chain-molecules being in position to attract each other. In this connection it may be noted that fillers also help to increase the strength of rubber compounds by attaching themselves to the uncoordinated polar groups.

## THE STRUCTURE OF POLYISOPRENES

### III. ULTRAVIOLET ABSORPTION SPECTRA \*

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Ultraviolet absorption measurements on polyisoprenes were carried out in 1927 by Scheibe and Pummerer<sup>1</sup>, who compared the optical behavior of rubber and gutta-percha with that of simple olefins. The considerable advances since made in correlating spectral data with molecular structure and in the theoretical interpretation of the electronic bands, together with experimental progress in the preparation and purification of hydrocarbons, now make a fresh survey desirable. Additional justification is derived from the recent discovery, reported in Part I of this series<sup>2</sup>, that the diisoprene derivative geranylamine hydrochloride exhibits a new type of hybrid bond character akin to conjugation<sup>3</sup>.

Isolated olefinic linkages give rise to intense absorption, beginning in the neighborhood of 2000 A.U., and rising steeply to a maximum near 1850 A.U., its precise location being governed by second-order environment effects<sup>4</sup>. This characteristic absorption band has been identified by Mulliken<sup>5</sup> as an  $N \rightarrow V$  transition from the normal to the first ionic excited state of the double bond. In conjugated systems it occurs at progressively longer wave-lengths and, in general, any change in electronic activation that affects the energy of the  $N \rightarrow V$  transition will be reflected both in a displacement of the actual maximum and in a corresponding shift of the area covered by the absorption band. Since polyisoprenes do not readily lend themselves to vacuum ultraviolet methods, our measurements were confined to solutions through quartz optics, a technique which fixes a lower wave-length limit of 2000 A.U., but offers the advantage of accurate intensity data in the accessible region of the steep near-ultraviolet slope of the spectrum.

#### EXPERIMENTAL

*Spectrographic technique and notation.*—A small Hilger quartz spectrograph (E 484) was employed, in conjunction with the Spekker photometer and a tungsten-steel spark source of ultraviolet light. The spectra were recorded on Kodak B-10 plates, and the match-points determined visually. Except where otherwise stated, pure cyclohexane was used as the solvent in cell lengths of 0.1 to 5.0 cm. Independent determinations carried out on separate samples of the same hydrocarbon provided confirmation that the probable error was less than 3 per cent, which is negligible on the steep portion of the absorption slope.

The molecular extinction coefficient  $\epsilon$  is defined by  $\epsilon = (M/lc) \log_{10} I_0/I$ , in which  $\log_{10} I_0/I$  at the matching wave-length is given directly by the drum-setting of the photometer, after allowance for a suitable blank;  $l$  is the cell-length in cm., and  $c$  the concentration (in g. per l.) of the dissolved substance of molecular weight  $M$ . The ethylenic extinction coefficient  $e = \epsilon/n$  is also

\* Reprinted from the *Journal of the Chemical Society*, pages 600-606, 1944. This paper is Publication no. 56 of the British Rubber Producers' Research Association.

employed in the study of the polyisoprenes and other compounds containing  $n$  double bonds to obtain comparable intensity values representing the absorption of one ethylenic linkage. With this convention the absorption of rubber is plotted per single isoprene residue, but that of isoprene itself as the absorption of the half-molecule.

*Preparation and purification of materials.*—1-*tert*-Butylcyclohexene is the only new compound to be described, but details are also given of the purification procedures adopted for those hydrocarbons whose low-intensity absorption bands are plotted in Figure 1. The preparative methods employed for the remaining materials not specially purified for low-intensity investigation are briefly summarized at the end of this section.

1-*tert*-Butylcyclohexene.—The reaction of *tert*-butylmagnesium chloride with cyclohexanone produced much undesired cyclohexanol (b. p.  $61^{\circ}/13$  mm.) and a poor yield of 1-*tert*-butylcyclohexanol (b. p.  $80^{\circ}/13$  mm.), which were separated in a Dufton column. This carbinol solidified almost immediately in the receiver (m. p.  $49$ – $50^{\circ}$ ), but was too soluble in the usual solvents to permit of recrystallization (found: C, 76.8; H, 12.9;  $C_{10}H_{20}O$  requires C, 76.95; H, 12.8%). Distillation of this from a few crystals of iodine readily gave 1-*tert*-butylcyclohexene (b. p.  $158^{\circ}/765$  mm.), which was kept over molten sodium for one hour and finally redistilled at  $51^{\circ}/14$  mm.;  $n_D^{61.5^{\circ}}$  1.4632 (found: C, 86.8; H, 13.2;  $C_{10}H_{18}$  requires C, 87.0; H, 13.0%).

*Spectrographically pure hydrocarbons.*—Except where otherwise stated, each specimen was distilled through all-glass, grease-free, fractionation apparatus of the Fenske-Whitmore type immediately before optical examination.

1-Pentene and 1,4-pentadiene were generated from their pure bromoethers which had been obtained by the method of Boord *et al.*<sup>6</sup> as modified by Kistiakowsky *et al.*<sup>7</sup> The hydrocarbon spectra underwent no further change after three azeotropic distillations with methyl alcohol (b. p.  $26.6^{\circ}$  and  $23.5^{\circ}$ , respectively), and the pure olefins boiling at  $30.1^{\circ}$  and  $25.8^{\circ}$  were isolated by repeated washings with ice-water.

The low-intensity absorption of 1,5-hexadiene, prepared from allyl bromide and magnesium, remained constant after three fractionations at  $59.1^{\circ}$ . Isoprene was similarly purified (b. p.  $33.87^{\circ}/758$  mm.) from the crude hydrocarbon obtained on alkaline distillation of its recrystallized sulfone (m. p.  $63.5^{\circ}$ ).

None of the cyclohexenes could be freed from traces of conjugated dienes by fractionation alone, but both cyclohexene and 1-methylcyclohexene were produced spectrographically pure on treatment with maleic anhydride<sup>8</sup>.

"Dihydromyrcene"<sup>9</sup> has been employed in chemical work as a representative of the diisoprenic 2,6-dimethyl-2,6-octadiene hydrocarbon<sup>10</sup>, but Dupont and Desreux<sup>11</sup> obtained Raman spectra evidence that the reduction of  $\beta$ -myrcene invariably results in a certain amount of 1,2- as well as 1,4-addition of hydrogen. Apart from this objectionable complication, the spectra of our dihydromyrcene samples also exhibited the typical aromatic band system of *p*-cymene<sup>12</sup>, an impurity which could not be removed by fractionation. 2,6-Dimethyl-2,6-octadiene was therefore made by the reduction of purified geraniol with sodium in liquid ammonia<sup>13</sup>, and we are indebted to F. Hilton for this preparation. On careful fractionation, the pure hydrocarbon distilled at  $61.2^{\circ}/16$  mm.;  $n_D^{19.5^{\circ}}$  1.4498.

Rubber hydrocarbon was purified down to constant low-intensity absorption by a special precipitation method of fractionation, details of which will be given elsewhere. The final specimen contained 0.01 per cent of nitrogen, and had a viscosity molecular weight of  $330 \times 10^3$ .

*Preparation of other materials.*—1,2-Dimethylcyclohexene was obtained by condensation of methylmagnesium iodide with 2-methylcyclohexanone and dehydration of the tertiary carbinol product with iodine. After purification *via* the crystalline dibromide (m. p.  $142^{\circ}$ ), the hydrocarbon had b. p.  $135^{\circ}$ ,  $n_D^{12} 1.4591$ .

Geranylamine hydrochloride<sup>14</sup> was crystallized four times from acetone (m. p.  $146^{\circ}$ ) and dried in a vacuum. Oxidation impurities were removed from squalene hydrocarbon by adsorption on a column of alumina. Pure white Tjipetir gutta-percha<sup>15</sup> had N, 0.01%, and a viscosity molecular weight of  $78 \times 10^3$ .

### DISCUSSION

*Low-intensity long-wave absorption of olefins.*—It was noted by Carr and Walker<sup>16</sup> that even highly purified specimens of hydrocarbons containing iso-

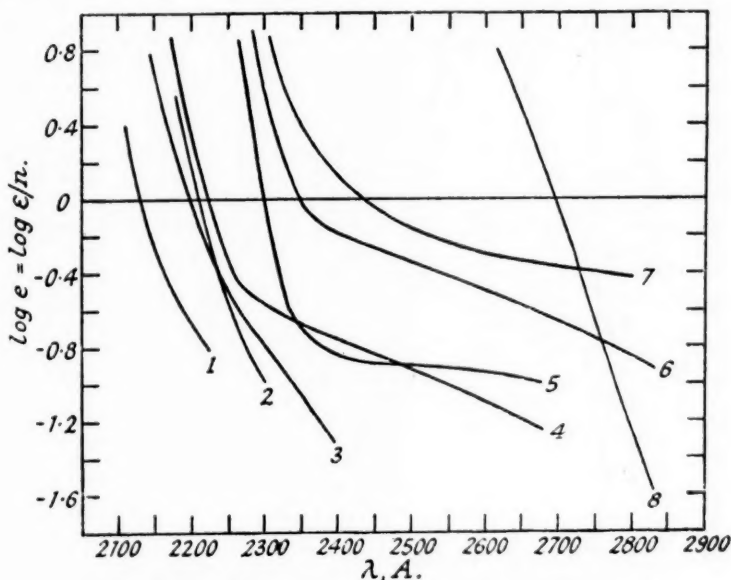


FIG. 1

- |                    |   |
|--------------------|---|
| 1. 1,5-Hexadiene.  | 5. 2,6-Dimethyl-2,6-octadiene.                  |
| 2. 1-Pentene.      | 6. 1-Methylcyclohexene.                         |
| 3. 1,4-Pentadiene. | 7. Rubber (in $C_6H_{12}$ containing 10% EtOH). |
| 4. Cyclohexene.    | 8. Isoprene.                                    |

lated ethylenic linkages regularly showed characteristic long-wave absorption tails in addition to the intense  $N \rightarrow V$  bands occurring at shorter wave-lengths. We have confirmed the presence of this weak absorption region in 1-pentene and in cyclohexene,<sup>8</sup> and we also observed its existence in spectrographically pure preparations of 1,5-hexadiene, 1,4-pentadiene, 1-methylcyclohexene, 2,6-dimethyl-2,6-octadiene, and rubber (Figure 1). The electronic process responsible for the long-wave ethylenic band has not yet been identified, but is of real significance as it must evidently play an important role in the photochemistry of these substances under sunlight conditions. Carr and Walker

have already directed attention to the marked increase of this absorption region associated with alkyl substitution of the double bond, and it can be seen from the figure that both methylcyclohexene and rubber actually absorb more strongly than the conjugated isoprene at wave-lengths longer than 2750 A.U.

Most of the olefinic spectra reported from Carr's laboratory also displayed

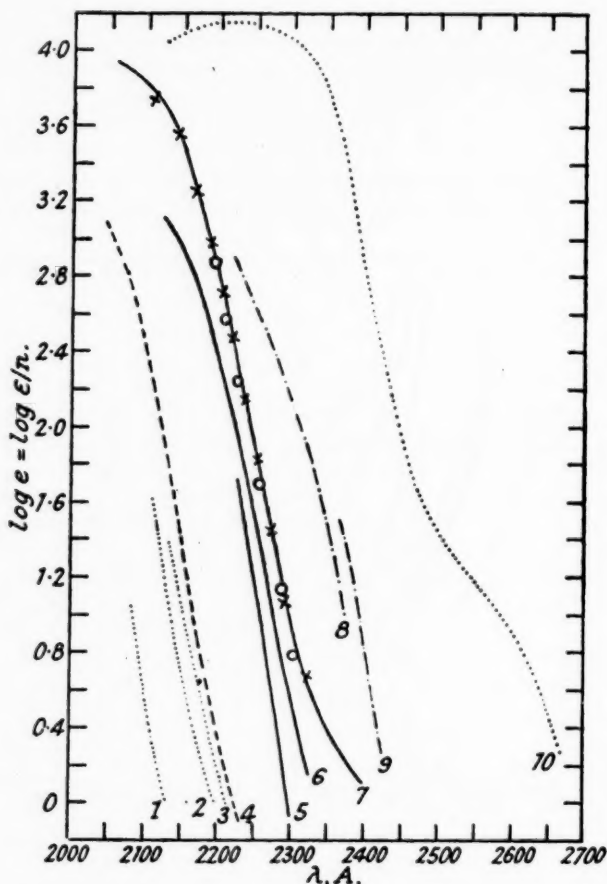


FIG. 2

1. 1,5-Hexadiene.
2. 1,4-Pentadiene.
3. 1-Pentene.
4. Cyclohexene.
5. 2,6-Dimethyl-2,6-octadiene.
6. 1-Methylcyclohexene.

7. Rubber (in  $C_6H_{12}$  containing 10% EtOH).
- × × ×. Gutta-percha.
- ○ ○. Squalene.
8. 1,2-Dimethylcyclohexene.
9. Tetramethylethylene<sup>16</sup>.
10. Isoprene.

inflexions or stepouts of varying intensity in the region of 2300 A.U. We encountered similar features in our own hydrocarbon specimens before systematic fractionation, which revealed that this type of band is caused by minute traces of intensely absorbing contaminants of a conjugated diene structure. Such irregularities are, therefore, not to be regarded as characteristic of pure olefin spectra, as was indeed suspected by the American authors.

*Classification of intense polyisoprene absorption.*—The extreme quartz ultraviolet spectrum of the polyisoprenes is compared with that of some related olefins in Figure 2. The complete coincidence of the absorption curves of rubber and gutta-percha is of interest in view of the geometrical isomerism which is believed to distinguish these two hydrocarbons. Ramart-Lucas<sup>17</sup> has, however, already refuted earlier assertions that there existed a systematic difference between the ultraviolet spectra of *cis-trans*-isomeric absorbing groups,

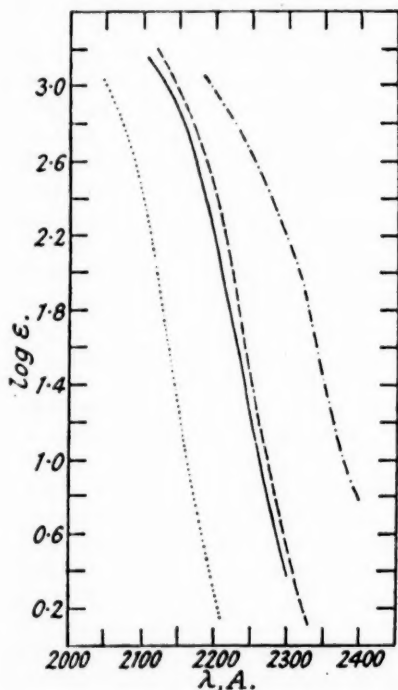


FIG. 3

..... Cyclohexene.  
 — 1-tert.-Butylcyclohexene.  
 - - - 1-Methylcyclohexene.  
 - · - 1,2-Dimethylcyclohexene.

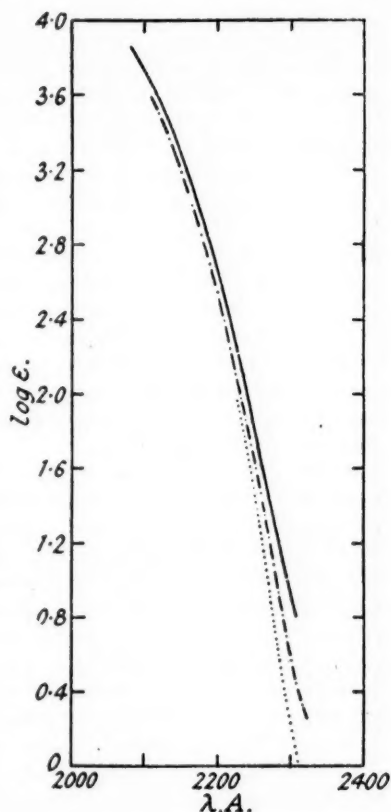


FIG. 4

— Geranylamine hydrochloride (diisoprene amine hydrochloride) in EtOH.  
 - - - 2,6-Dimethyl-2,6-octadiene (diisoprene) in EtOH.  
 ..... Geranylamine hydrochloride (diisoprene) in C<sub>6</sub>H<sub>12</sub>.  
 - · - 2,6-Dimethyl-2,6-octadiene (diisoprene) in C<sub>6</sub>H<sub>12</sub>.

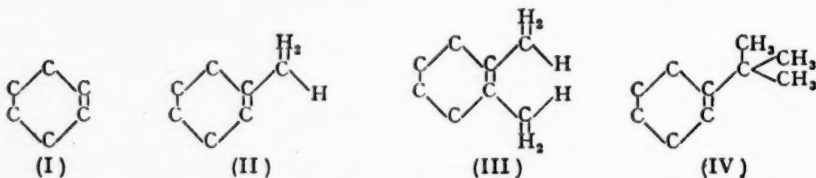
and the high-intensity  $N \rightarrow V$  absorption of the two forms of 2-butene appears to occur at the same wave-lengths<sup>18</sup>. Most of the existing spectrographic data on pairs of geometrical isomers relate to more complex chromophores than the simple alkyl-substituted ethylenic linkage, and the reduced absorption usually displayed by the *cis*-isomerides can be attributed to their shortened spatial extension or to steric interference between *cis*-ethylenic substituents<sup>19</sup>. The polyisoprene curves also cover our measurements on squalene and is

identical with the earlier data on rubber and gutta-percha obtained by Scheibe and Pummerer<sup>1</sup>, whose curve for diallyl is likewise confirmed.

The figure shows that the spectra of the polyisoprenes and other unsaturated hydrocarbons of the trisubstituted type  $CR_1R_2:CHR_3$  form a well-defined group, clearly differentiated from all other ethylenic compounds, which are either more or less absorptive in accordance with the extent of substitution on the double bond. The precise nature of the alkyl substituents appears to be largely immaterial in this classification, provided that no conjugation occurs when more than one double bond is present in the molecule (cf. spectrum of isoprene). Carr and Walker<sup>16</sup> and Price and Tutte<sup>20</sup> previously observed corresponding red shifts in the vapor spectra of some simple ethylenes in the vacuum ultraviolet. Analogous long-wave alkylation displacements are also known to occur in the spectra of the conjugated dienes<sup>21</sup> and of olefinic centres conjugated with a carbonyl group<sup>22</sup>.

Although the absorption of 1,5-hexadiene at the extreme short-wave end of the quartz ultraviolet is in line with this classification, yet the spectra of the monosubstituted ethylenes 1-pentene and 1,4-pentadiene appear to lie remarkably close to the curve of cyclohexene, which is more highly substituted on the double bond. According to Carr and Walker<sup>16</sup> who record different absorption values for 1-pentene, isopropylethylene is even more absorptive than cyclohexene in this region. Since the peak of the isopropylethylene band is reported to fit normally into its group position<sup>18</sup>, it seems possible that the irregular spreading-out of the monosubstituted ethylene absorption curves may be due to a peculiar broadening or intensification of the band rather than a genuine wave-length shift.

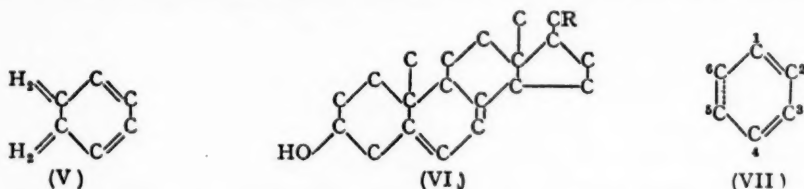
*Alkyl shifts and hyperconjugation.*—Mulliken<sup>23</sup> developed the theory of hyperconjugation to account for the abnormal long-wave absorption of cyclic conjugated dienes, and used it subsequently to explain the successive absorption shifts effected by alkyl substitution in simple ethylenes. The theory has been generalized and expressed quasi-quantitatively in quantum-mechanical terms, although some of the original views have been drastically revised<sup>24</sup>. Hyperconjugation, which is now considered to find expression in the properties of the ground state rather than those of excited states, is still regarded as determining the red shifts, although decreases in ionization potential are mainly attributed to charge transfer.<sup>5</sup> Since the conjugated powers of saturated bond electrons with unsaturated centres is much greater for C—H than for C—C bonds, the long-wave displacements in the cyclohexene series are due, on this view, to the increasing conjugation inherent in structures (I)–(III). We have



been able to test this theory experimentally by examining 1-*tert*-butylcyclohexene (as IV) in which all the side-chain hydrogen atoms necessary for hyperconjugation have been replaced by carbon. The spectrum of this new olefin is given in Figure 3, and comparison with methylcyclohexene and other cyclohexenes proves that alkyl shifts are predominantly a function of carbon sub-

stitution as such, irrespective of the presence or otherwise of C—H bonds in the substituent group. This result is comparable with Conant and Kistiakowsky's heat of hydrogenation data<sup>25</sup> in which negligible differences between methyl-, ethyl-, isopropyl-, and *tert*-butylethylene were found.

Differing from Mulliken, Price and Tuttle<sup>20</sup> regard alkyl displacements as chiefly due to a reduction in ionization potential of the ethylenic center by charge transfer from the adjacent alkyl groups, a process which should lead to parallel changes in heats of hydrogenation. In conjugated cyclohexadiene the  $N \rightarrow V_1$  transition occurring at much longer wave-lengths than in the open-chain dienes is similarly related to an alteration in the ground state. If this is correct, it seems remarkable that its heat of hydrogenation does not differ appreciably from that of an analogous butadiene<sup>25</sup>. Mulliken's alternative explanation of the cyclohexadiene spectrum is open to more serious objection from arguments based on chemical constitution. If hyperconjugation depicted in structure (V) is regarded as determining the red shift from the normal conjugated diene spectrum, then it is difficult to see why substituted cyclohexadienes of the type of ergosterol (VI) should absorb at even longer wave-lengths. In point of act, all the spectrographic data on polycyclic dienes have been accumulated in recent years<sup>26</sup> serve to show that the incorporation



of the conjugated diene system in one six-membered ring is the exclusive cause of the abnormal spectrum regardless of all second-order substitutional influences.

It has been shown beyond doubt that hyperconjugation is an important mechanism of electronic activation in chemical processes<sup>27</sup>, and physical measurements have indicated its influences in the ground state<sup>28</sup>; but it is evident that the spectral features of hyperconjugation have yet to be correctly described.

*Interaction of double bonds in the polyisoprene chain.*—There is a generally accepted working hypothesis in ultraviolet spectroscopy that two chromophores contained in the same molecule behave as separate absorbing entities, provided they are separated by one or more carbon atoms (Ramart-Lucas, *loc. cit.*) This is borne out by our data on 1,4-pentadiene, 1,5-hexadiene, and the polyisoprenes, all of which fall into their normal group classification in accordance with the degree of alkyl substitution of the double bond. The spectrographic rule is paralleled by the available thermal data, since the heat of hydrogenation of 1,5-hexadiene is almost identical with twice that of a singly substituted ethylene, and the same is very nearly true of 1,4-pentadiene<sup>7</sup>. The only exception that might be quoted against this generalization is the spectral anomaly of the cyclic conjugated dienes. Although Price and Walsh<sup>29</sup> tentatively postulated electronic repulsion between the two *cis*-linked double bonds, or, alternatively, the existence of Dewar type resonance structures in 1,3-cyclohexadiene, yet Woodward<sup>30</sup> envisaged an incompletely insulating 5, 6 single bond in a benzene-analogous structure (VII). This formulation would account for the long-wave absorption, but the normal heat of hydrogenation remains a difficulty.

Recent physical evidence points to incomplete insulation of the 1,5-spaced double bonds in the polyisoprene chain, comparable with that represented in structure (VII). X-ray analysis of the diisoprene derivative, geranylamine hydrochloride,  $\text{CMe}_2\text{:CH}\cdot\text{CH}_2=\text{CH}_2\cdot\text{CMe}\text{:CH}\cdot\text{CH}_2\cdot\text{NH}_2$ ,  $\text{HCl}^{31}$ , has revealed a significant shortening of the central single bond, accompanied by a planar arrangement of the adjacent groups. It has been suggested<sup>32</sup> that this unique bond character, which simulates normal conjugation, is the result of hyperconjugation. The ethylenic centres are considered to promote hybridization which partially localizes the C—H bond electrons of the central  $\text{CH}_2$  groups in the hybrid bond. It is perhaps surprising therefore that the  $\text{N} \rightarrow \text{V}$  band of the polyisoprenes does not reflect this structural modification and that the spectrographic insulation rule still holds. There is no difference in this respect between diisoprene itself and its amine hydrochloride, whose spectra are plotted side by side in Figure 4. Since saturated amine hydrochloride groups are completely transparent in the quartz ultraviolet, the absorption of geranylamine hydrochloride in this region is determined exclusively by the diisoprene system, and the close coincidence of the two spectra is very striking.

The latter observation is of further interest because of its bearing on the inductive dependence of  $\text{N} \rightarrow \text{V}$  transitions.<sup>33</sup> Price and his colleagues conclude that the determinative function of alkyl substituents at ethylenic centres is one of charge transfer, which they identify with the inductive mechanism well recognized chemically. Now, it is well known that a substantial fraction of the electrostatic force of an ionic pole is transmitted through one saturated carbon atom. Hence at the nearer double bond in geranylamine hydrochloride there will be an added inductive influence of marked strength directly the same as that of the methyl substituent. Moreover, it is not possible in this case to invoke an alternative and compensating mode of polarization as in *cis*-dichloroethylene and chloroprene, where correlation between spectral displacement and the inductive power of the chlorine atom was also absent<sup>34</sup>, and we must conclude that double bond absorption is far less sensitive to inductive influence than hitherto believed.

There appear to be three possible explanations why the spectrum of geranylamine hydrochloride shows no departure from that typical of a substituted ethylene in spite of the unusual character of the central single bond. First, the abnormal bond may be peculiar to the crystalline state; secondly, the presence of the ethylenic centres may not in fact govern the new hybridization. We see no reason for accepting the former, and regard the latter as improbable. Thirdly, both normal and excited states of the double bond may participate equally in the hyperconjugation process, in the same way, presumably, as they are similarly responsive to the polar force of the ammonium group. However, this problem of unchanged transition energy must remain unsolved until the true spectral consequence of hyperconjugation is elucidated, and the nature of the unusual hybridization more fully understood.

#### SUMMARY

The quartz ultraviolet absorption spectra of highly purified polyisoprenes correspond closely to those of simple ethylenes having the same degree of alkyl substitution at the double bond. This is also true of geranylamine hydrochloride, which shows no obvious characteristic that can be identified with the structural anomaly revealed by x-ray crystal analysis. The extent to which spectral variations are a measure of the electronic properties of groups and

molecules of this type is therefore discussed—with the conclusion that for formally saturated substituents the correlation is still obscure. Evidence is presented to show that inductive influence is slight, and that interpretations hitherto advanced on the basis of hyperconjugation are unsound.

### ACKNOWLEDGMENT

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## PLASTICITY MEASUREMENTS IN THE RUBBER INDUSTRY. IV\*

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Several years ago, Höppler published some plasticity measurements<sup>1</sup> made with an apparatus which he had just then developed. This work is of particular interest because his curves, which record plasticity values in the absolute system for various pressures and temperatures, resemble very closely some curves which the present author derived from data<sup>2</sup> obtained with a Marzetti plastometer, *i.e.*, with an entirely different type of apparatus. It is only reasonable to conclude that similar phenomena were measured by the two different instruments.

It has been customary in the past to express measurements obtained with an extrusion plastometer in terms of Marzetti units, *i.e.*, as the square root of the number of cubic centimeters of material extruded in a 15-minute interval<sup>3</sup>. In this case the pressure and the temperature must be taken into account. In the present work it is attempted, with the help of data already available, to develop a formula which expresses plasticity values in the c.g.s. system for the extrusion plastometer.

Since an extremely wide variety of mixtures is to be found in the rubber industry, a large number of such mixtures must be studied to obtain a clear picture of their general behavior. In the rapid plastometric method developed by the present author<sup>3</sup>, the dependence of the rate of flow on the temperature and pressure was first investigated. The data are recorded in Table 1 and in Figures 1 to 5. In these diagrams the data are plotted on a double logarithmic scale, since in a previous investigation<sup>3</sup> it was shown that when plotted in this way, straight lines which conform to the following equation are obtained:

$$v_{15} = Ct^n \quad (1)$$

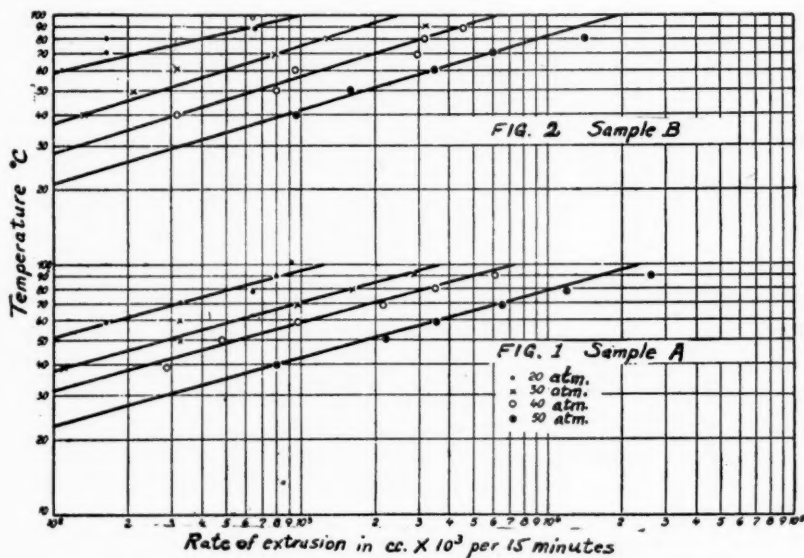
where  $v_{15}$  is the rate of extrusion in cc.  $\times 1000$  per 15 minutes,  $C$  and  $n$  are constants, and  $t$  is the temperature (Centigrade).

Five different materials were tested: (1) slightly degraded Buna-S; (2) highly degraded Buna-S; (3) slightly masticated smoked-sheet rubber; (4) highly masticated smoked-sheet rubber; and (5) a Buna-S tire-tread mixture containing 45 per cent of carbon black.

It is obvious that the distances of the straight lines from the zero point differ greatly, depending both on the composition of the mixture and on the pressure. This means, in terms of Equation (1), that constant  $C$  has different values. On the other hand, constant  $n$  does not in general change as the pressure is increased, but shows fairly uniform values in all of the five cases shown in Table 2.

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk*, Vol. 20, pages 15-19, May-June 1944. For Parts I, II and III of this series, see *Kautschuk*, Vol. 8, p. 2 (1932); Vol. 8, p. 167 (1932), and Vol. 15, p. 112 (1939), respectively. Parts I and II appear also in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 6, pp. 244-260 (1933).

In judging the significance of the values recorded in Table 2, it must be taken into consideration that a difference of 0.5 represents a difference of approximately  $2^\circ$  in the slope of the straight lines, and that this difference lies within the limit of error inherent in the rapid plastometer method as developed for technical use. It can, therefore, be said that the inclinations of the lines representing mixtures A, B and D are approximately the same, and that constant  $n$  has a value of approximately 4. Only the values for mixtures C and E differ considerably from those for mixtures A, B and D. Slightly masticated smoked sheet (mixture C) shows a relatively high temperature exponent, *i.e.*, with increase in temperature the mobility of the macromolecules increases much more than does the mobility of the macromolecules of highly masticated smoked-sheet rubber (mixture D) or of thermally softened Buna-S (mixtures A and B).



FIGS. 1-2.

This difference in behavior can be best explained, perhaps, by referring to the views set forth by Ueberreiter<sup>4</sup>. According to the latter, a sharp distinction must be made between intermolecular forces and intramolecular forces when the temperature of macromolecular substances is raised. As the temperature rises, the intramolecular forces are first overcome, and the chain members become mobile. Only at much higher temperatures do the macromolecules themselves become mobile, and the temperature range between these two phenomena depends on the chain length of the macromolecules. Applied to the present work, this means that, within the temperature range of  $40^\circ$  to  $90^\circ\text{C}$  which was investigated, the intramolecular forces are small in thermally softened Buna-S and also in highly masticated natural rubber (mixtures A, B and D). The thermal energy is, therefore, consumed to a great extent in overcoming the intermolecular forces; in other words the thermal energy serves to increase the internal mobility of the macromolecules. On the

contrary, in the case of slightly masticated natural rubber a "liquid with fixed structure", to quote Ueberreiter, is involved throughout the temperature range, and this makes it understandable why the temperature coefficient is so much higher than the coefficients of the other samples; in brief, the energy consumed is expended only in overcoming the intramolecular forces.

TABLE 1  
RATES OF FLOW OF VARIOUS SAMPLES AS A FUNCTION OF THE  
PRESSURE AND TEMPERATURE  
(Volume in cc. 1000 extruded in 15 minutes)

Temperature	Sample	Pressure in kg. per sq. cm.				
		10	20	30	40	50
40° C	A	54 (44° C)	54 (42° C)	107.5 (39° C)	290 (39° C)	807
	B	54 (42° C)	54	134.5	322	966
	C	0	>0	54 (41° C)	107.5 (41° C)	242
	D	54	107.5 (39° C)	161	1880 (40° C)	6940
	E	>0	42 (41° C)	252 (41° C)	378	1050
50° C	A	54 (50° C)	80.5 (50° C)	322	484 (49° C)	2260
	B	50 (48° C)	80.5	215 (49° C)	806 (49° C)	1615
	C	0	107.5	322 (51° C)	484 (49° C)	2260
	D	322	2266 (51° C)	8720 (51° C)	25800	72000
	E	42	84	694	1135	4420
60° C	A	>0	162 (59° C)	322	970 (59° C)	3540 (59° C)
	B	>0	107.5	322 (61° C)	970	3540
	C	>0	270	970	4200	14500
	D	890	4525	16800	46000	176000
	E	42	252 (61° C)	1135	5040	19700 (62° C)
70° C	A	>0	322 (71° C)	970 (69° C)	2100 (69° C)	5460 (69° C)
	B	>0	162	806 (69° C)	3060 (69° C)	6130
	C	>0	322 (69° C)	640 (69° C)	3220 (68° C)	12600 (68° C)
	D	1050 (71° C)	7100	26400 (69° C)	77500	300000
	E	42 (69° C)	630	2020 (71° C)	6380 (69° C)	26500 (69° C)
80° C	A	>0	645 (79° C)	1615 (79° C)	3560	11950 (79° C)
	B	>0	163	1290 (80° C)	3240	14200 (81° C)
	C	54 (79° C)	322 (78° C)	1130 (79° C)	3250 (78° C)	22000 (79° C)
	D	1210	7750 (79° C)	28800 (78° C)	74600 (78° C)	325000 (78° C)
	E	63 (79° C)	1010 (78° C)	2410 (79° C)	8060	30300
90° C	A	54	810 (89° C)	2900 (81° C)	6130	26800
	B	215	645 (89° C)	3220	4680 (88° C)	126000 (88° C)
	C	215 (89° C)	1130 (88° C)	3560 (88° C)	12200 (89° C)	62300
	D	2260	10420 (89° C)	36800 (88° C)	95000 (88° C)	392000
	E	63 (91° C)	9700 (90° C)	2400	8550 (89° C)	37400 (89° C)

Samples:

- A Buna-S, degraded 90 min. at 130° C at atmospheric pressure, tested after 1 month.
- B Buna-S, degraded 50 min. at 130° C at 3 atmospheres air pressure, tested after 7 months.
- C Smoked sheet, masticated 4 min., tested after 24 hrs.
- D Smoked sheet, masticated 20 min., tested after 24 hrs.
- E Buna-S tire-tread mixture ( $d = 1.19$ ).

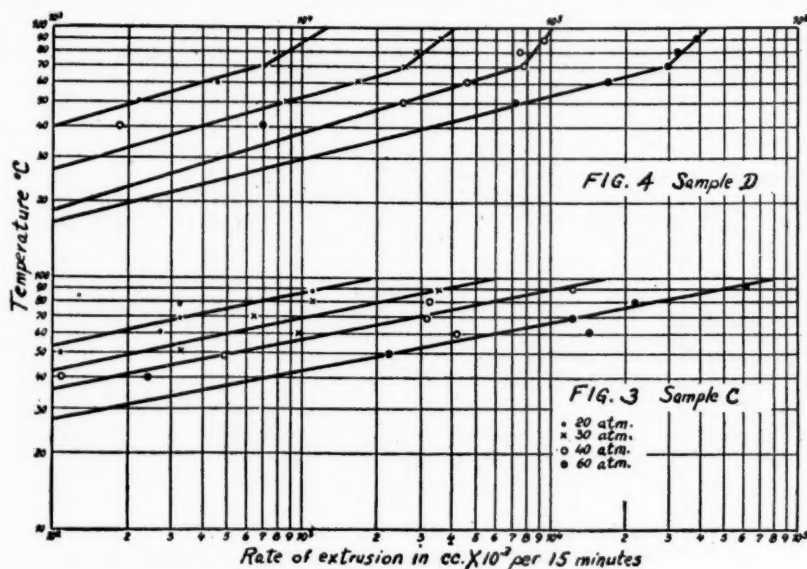
TABLE 2  
CONSTANT  $n$  AT DIFFERENT PRESSURES

Pressure (kg. per sq. cm.)	Mixture				
	A	B	C	D	E
20	4.0	3.5	5.7	3.5	5.7
30	4.0	3.5	5.7	3.5	4.0
40	4.0	3.5	5.7	3.5	7.1
60	4.0	3.5	5.7	4.0	7.1

These same relations hold true of loaded rubber mixtures, provided that the latter contain little or no active filler. Data on such systems are recorded in Table 4 and in Figures 13 and 14. Here too constant  $n$  is approximately 4. Mixtures containing active fillers behave otherwise. A tire-tread mixture (sample E) is chosen as an example of such mixtures. At a pressure of 20

kg. per sq. cm. the temperature exponent is higher than normal; at a pressure of 30 kg. per sq. cm. it reaches the value of 4; and at pressures of 40–60 kg. per sq. cm. it increases to very high values. This remarkable behavior may be explained in the following way.

Mixtures containing active fillers are fairly rigid at room temperature, but with increase in temperature there is a greater increase in the mobility of the macromolecules than in the case of pure rubber or of rubber mixtures containing inert fillers. In other words, an increase in temperature not only increases the mobility of the rubber molecules, but also loosens the bond between rubber and carbon black. Now the extremely fine carbon black, together with softeners, which are present, is a far more effective lubricating agent than is a relatively coarse inert filler. That such a system should possess more plastic flow at any given temperature than normal rubber is quite understandable. A



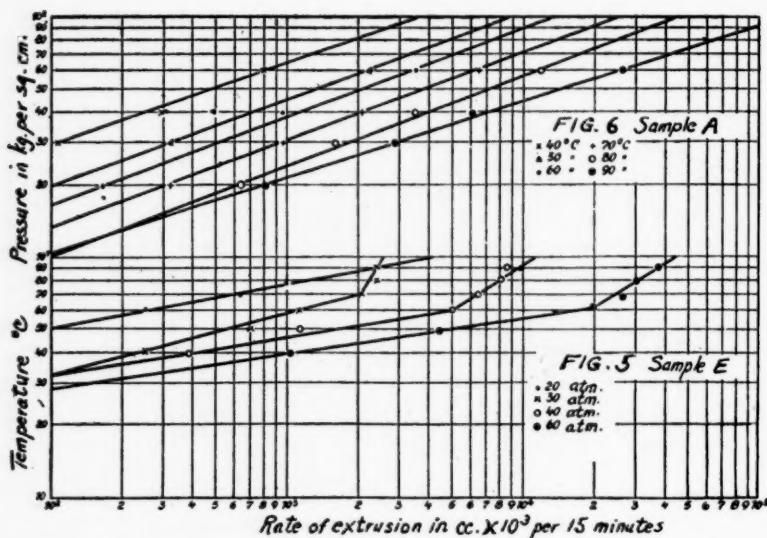
FIGS. 3-4.

comparison of the data in Table 1, as well as in Figures 1 to 5, shows this very plainly. All this is true when the pressure is 20 kg. per sq. cm. If the pressure is raised gradually, a temperature is reached, which is lower than in the first series of experiments, at which the bond between rubber and carbon black is broken. From this point on, an increase in temperature serves only to loosen the bonds between rubber molecules. As a result the temperature exponent again becomes normal. This is the case when mixture E is under a pressure of 30 kg. per sq. cm. Unexpectedly the temperature exponent again becomes greater when the rubber mixture is extruded under a pressure of 40 or 60 kg. per sq. cm. This cannot be explained at present.

It is worthy of note that the straight lines of mixtures D and E (see Figures 4 and 5) change their directions at elevated temperatures, *e.g.*, mixture D at 70° C, as a result of which the  $n$  value decreases from 1.6 to 0.75. This means in other words that, above this critical temperature, the velocity of extrusion

does not increase at the same rate as it does below the critical temperature. This anomaly is probably explained by assuming that, at relatively high temperatures, extensive agglomeration of the rubber or of its compounding ingredients takes place, and that this inhibits plastic flow. In the case of mixture E, this must be regarded as the first stage of incipient vulcanization. It should be mentioned at this point that, at a pressure of 20 kg. per sq. cm., this mixture does not show a break in its curve. There is no explanation for this unless it is assumed that the sample chosen for the experiment had less tendency to reach the stage of incipient vulcanization than did the other samples because of uneven dispersion of accelerator and consequent inhomogeneity.

This explanation that incipient vulcanization is involved does not hold true of mixture D, which consisted solely of highly masticated smoked-sheet rubber. As already mentioned, according to the views of Staudinger, the rod-shaped macromolecules of rubber are ruptured by mastication. These



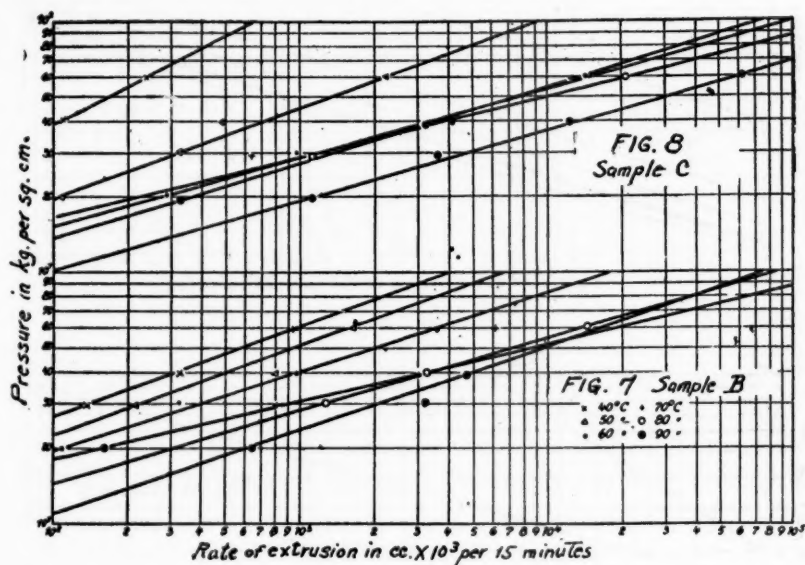
FIGS. 5-6.

fragments are naturally much more mobile than the original macromolecules; nevertheless, at low temperatures they obstruct one another to a considerable extent. With gradual warming, these associations become progressively looser, so that finally the system becomes virtually liquid. It is easy to see that, from this point on, a further rise in temperature does not increase the rate of extrusion to the same extent that it does within the range of temperature where rubber still behaves as a liquid with a fixed structure.

It is evident, therefore, that two entirely different properties of rubber are represented by the same curve in the temperature-rate of extrusion diagram. However, as will be seen later, although incipient vulcanization is likewise manifest in the pressure-rate of extrusion diagram as a change in direction of the straight line, this is not the case with highly masticated rubber. In this way it is possible to distinguish the two phenomena from one another. Actually, however, this liquefaction of rubber occurs only rarely in present-day

technical practice, although it might often have happened in the past in processing wild rubbers and native rubbers. It was found, in fact, that, by prolonged mastication such as is necessary in the manufacture of sponge rubber, the rubber flowed from the mill rolls. In the plastometer this property is manifest by an unusually high rate of extrusion. As is evident in Figures 1 to 5, the rate of extrusion of mixture D is higher by a 10th power than the rates of the other samples.

To obtain a better idea of the dependence of the rate of extrusion on the pressure, the data in Table 1 are plotted in Figures 6 to 10, in this case too on a double logarithmic scale.



FIGS. 7-8.

The straight lines conform to the following equation:

$$v_{15} = K \cdot p^m \quad (2)$$

where  $K$  and  $m$  are constants.

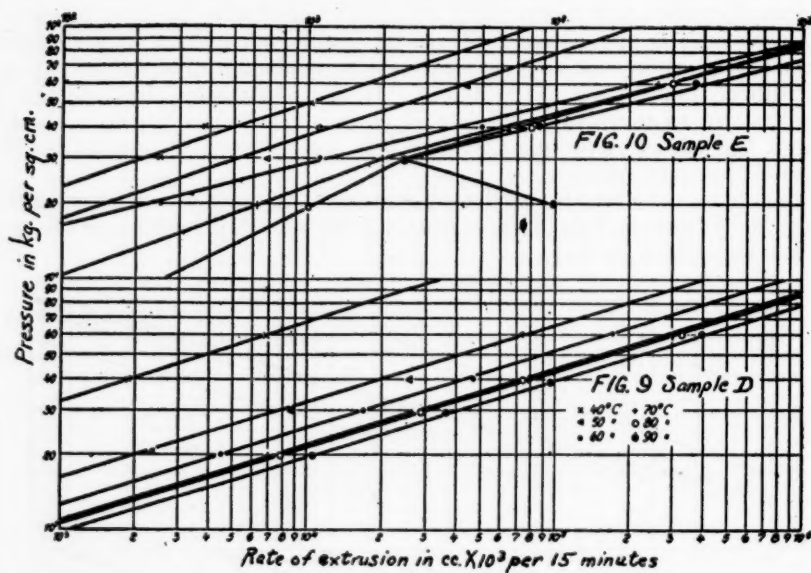
Table 3 shows the slopes of the straight lines in Figures 6 to 10 which, to distinguish them from the second constant in Equation (1), are designated by the symbol  $m$ .

The data in Table 3 show that slightly degraded Buna-S (mixture A) has a

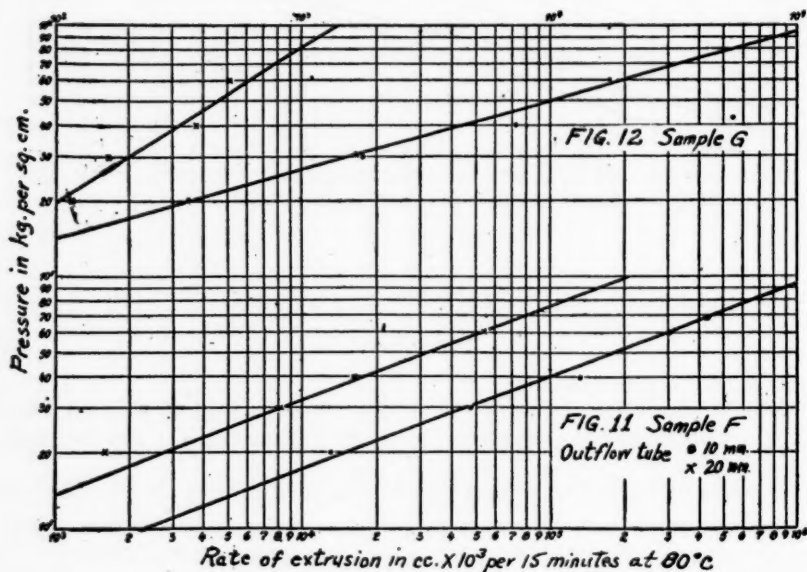
TABLE 3

Values of  $m$  for mixture

Temperature	A	B	C	D	E
40°	2.9	2.9	2.0	3.5	2.9
50°	2.9	2.9	2.9	3.5	3.5
60°	2.9	3.3	4.0	3.5	4.0
70°	2.9	4.0	3.5	3.5	2.9
80°	2.9	3.5	3.5	3.5	2.0
90°	3.0	2.9	3.5	3.5	—



FIGS. 9-10.



FIGS. 11-12.

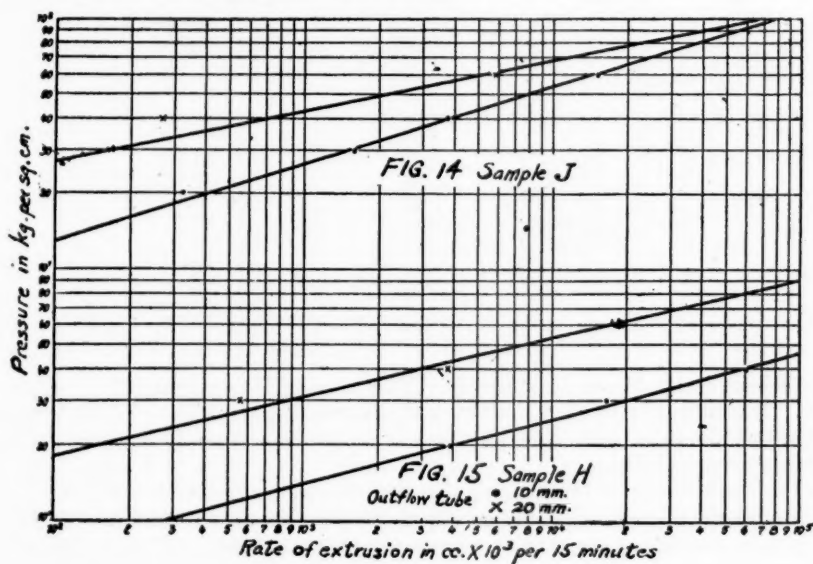
constant  $m$  value from 40° to 80° C, and only at 90° C increases slightly. However, this slight increase lies within the limits of experimental error.

Highly degraded Buna-S (Sample B) behaves far differently. In this case the pressure exponent shows an increase even at 60° C, but above 70° C

it decreases steadily until, at about 90° C, it reaches its original value of 2.9. Because of the relatively advanced state of degradation, the intermolecular forces have already become insignificant around 60° C, but with further increase in temperature, the macromolecules assume a network formation, and this network structure inhibits plastic flow, so that the pressure exponent again decreases.

The  $C$  value of slightly masticated smoked-sheet rubber at 40° C is lower than its  $m$  value; it increases up to 60° C, decreases to 3.5 at 70° C, and then remains constant with further rise in temperature. This phenomenon is explained in the same way as before, except that in this last case there is probably no network formation in the macromolecules.

It is interesting that the value of 3.5 again appears in the D series, in this case at as low a temperature as 40° C.



FIGS. 13-14.

Prolonged mastication of sample D ruptures the macromolecules to such an extent that thermal treatment no longer has any influence on the pressure exponent.

Reference to the data in Table 2 will show the behavior of sample E. Here loosening of the bond between rubber and carbon black by increase in temperature results in an increase in the value of  $m$ , while incipient vulcanization tends to decrease the value of  $m$ .

A study of the influence of the dimensions of the apparatus on the rate of extrusion seemed at this point very desirable, but unfortunately because of limitations of time it was found impracticable by the present author to study all factors involved in the phenomena. Nevertheless, a few experiments with two different lengths of outflow tube of the apparatus will be described (see Figures 11 to 14).

It is not possible to derive any law or general relation from the data in Table 4, and only the straight lines in Figures 11 and 13, by virtue of their

TABLE 4

Outflow in cc.  $\times 10^3$  in 15 Minutes at 80° C.

F smoked-sheet rubber (300 grams masticated for 20 minutes, and tested after 24 hours).

G Buna-S tire-tread mixture ( $d = 1.17$ ).

H Buna-S cable mixture (25 kg. strength).

J Buna-S cable mixture (100 kg. strength).

Length of tube (mm.) Pressure (kg. per sq. cm.)	F		G	
	10	20	10	20
10	7850 (83° C) 6800 (80° C)	645	43 (79° C) 45 (80° C)	21 (81° C) 20 (80° C)
20	13800 (81° C) 13200 (80° C)	1610	320 (78° C) 350 (80° C)	130 (82° C) 116 (80° C)
30	48800	8220	1670 (79° C) 1760 (80° C)	190 (82° C) 172 (80° C)
40	130200	16200	6800 (79° C) 7200 (80° C)	380
60	325000 (81° C) 310111 (80° C)	53400	17500	510

Length of tube (mm.) Pressure (kg. per sq. cm.)	H		J	
	10	20	10	20
10	160 (84° C) 134 (80° C)	72 95	22 (81° C) 21 (80° C)	0
20	4765 (84° C) 3950 (80° C)	95	328	traces
30	18720 (82° C) 17000 (80° C)	574	1420 (78° C) 1600 (80° C)	164
40	60200	3820	3610 (79° C) 3800 (80° C)	274
60	447000	19200	15340	5930

parallelism, indicate any dependence. The ratio of the constants  $C$  in Equation (1), which obey this law, serves as a measure of the influence of the length of the outflow tube, since this difference in length was the only variable in the two sets of apparatus.

The inconstancy of the ratio of  $C_{10}$  to  $C_{20}$  makes it evident that there are no fundamental and invariable constants of the apparatus, but that the rate of extrusion depends also on the composition of the sample. This is still more evident from the results obtained with Sample G and Sample J, in which case

TABLE 5

Sample	C 10	C 20	C 10/20
F	2250	430	5.25
H	280	8.2	34

the angles of inclination of the straight lines are decidedly different. The dependence of the rate of extrusion on the length of the outflow tube is, therefore, still more complicated. It is intended to return to this subject later when more data are available.

For comparison the data obtained by Marzetti<sup>5</sup> with masticated first-latex crepe are shown in Table 6.

The data in Table 6 are derived from the diagram in the paper of Marzetti, and are converted into cu. mm. Because of the small scale of this diagram, the data could be estimated in only an approximate way (see Figures 15 and 16). From these curves, the data in Table 7 were calculated.

TABLE 6  
RATE OF EXTRUSION IN CC. X 1000 PER 15 MINUTES

Pressure in kg. per sq. cm. Temperature (°C)	5	10	15	20
40°	—	27	107.5	154
50°	27	107.5	154	350
60°	69	430	1320	2900
70°	154	840	2500	5450
80°	350	1480	3860	8650
90°	430	2280	5600	12000
100°	678	3050	7750	15500

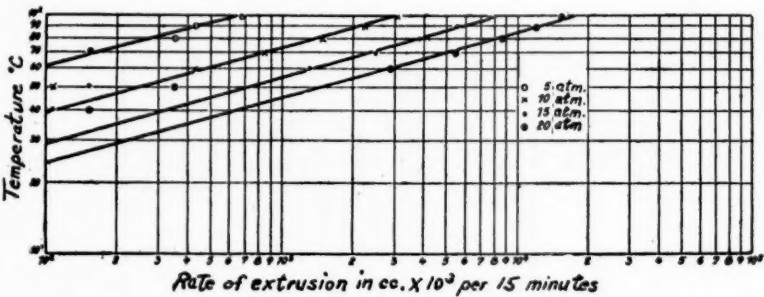


FIG. 15.

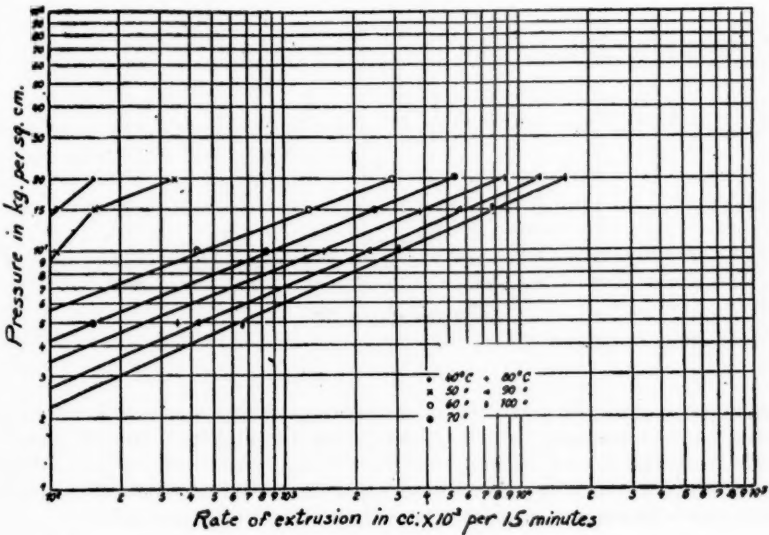


FIG. 16.

TABLE 7

Temperature	60° C.	70° C.	80° C.	90° C.	100° C.
<i>m</i>	2.75	2.6	2.5	2.4	2.3
<i>n</i> 3.7					

The values in Table 7 are approximately the same as those obtained by the present author. The contrary results of Marzetti, which indicate that the rate of extrusion is proportional to the square of the pressure, can be explained by the fact that Marzetti measured the quantity of material extruded on a basis of weight and, in addition, expressed the results in a simple coördinate system, whereas in the present work the results are expressed in terms of volume and are plotted on a logarithmic scale.

It should be mentioned further that the time factor in these experiments was taken into account only to the extent of assuming that the rate of extrusion remains constant when  $t$  and  $p$  are maintained constant. Actually this is not exactly the case; for with low values of  $t$  and  $p$ ,  $v$  was zero in these particular

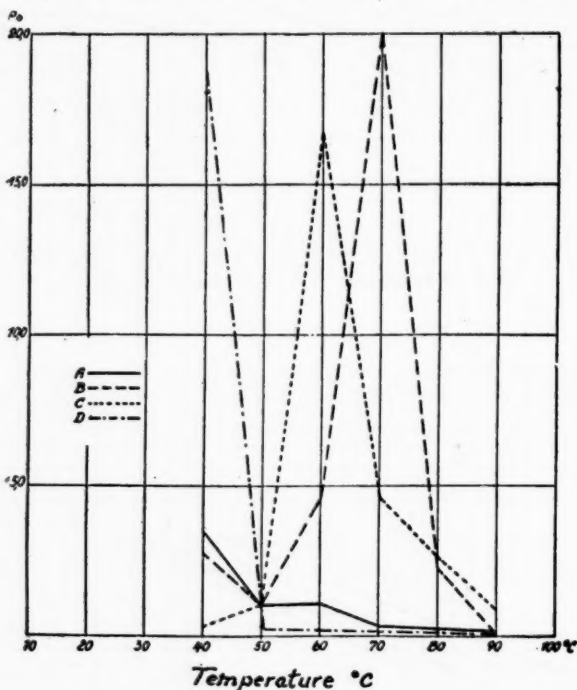


FIG. 17.

measurements, and the quantity of material extruded was small even after prolonged measurements. Furthermore, even for higher values of  $t$  and  $p$ , the rate of extrusion was not quite constant, but increased somewhat, although this was found to be true when the measurements were continued beyond 15 minutes, and therefore to a point where they played no great part.

Finally it should be noted that the thickness of the extruded cord depends on the pressure, temperature, composition of the material extruded, and degree of mastication of the rubber. Many mixtures swell considerably, especially those which are loaded but little, or in which the rubber or Buna has been masticated or degraded only slightly. It has been assumed that differences in thickness are a direct measure of the so-called nerve of the rubber. However, measurements by the present author show that this is not the case, probably

because no state of equilibrium exists. That there is some relation was proved years ago by the author in conjunction with Bachmann and Blankenstein<sup>6</sup>. The method described at that time, which can be regarded as a measurement of the surface tension of plastic materials, is based on a determination of the balance between gravitation and the surface tension of vertically suspended extruded cords. Since this test takes a very long time, another method was developed later<sup>2</sup>. This latter method involved a determination of the pressure  $p_0$  at which plastic flow sets in, *i.e.*, a determination of the yield value of Bingham<sup>7</sup>. It was shown at that time that this  $p_0$  value bears a simple relation to the nerve of the rubber.

The determination can be carried out in such a way that the straight line in the logarithmic  $v - p$  diagram is extrapolated to the point where it cuts the  $p$ -axis. It is simpler, however, to calculate  $p_0$ . If  $c/p_0$  is substituted for  $K$  in Equation (2), where  $c$  is a constant, then:

$$p_0 = c \frac{p^m}{v_{15}} \quad (3)$$

Values of  $p_0$  can be derived from Figures 6 to 9, and these are shown<sup>8</sup> in Table 8 and Figure 17.

TABLE 8  
VALUES OF  $p_0$  AT DIFFERENT TEMPERATURES  
Pressure 30 atmospheres;  $c = 3 \times 10^{-2}$

Sample	40° C	50° C	60° C	70° C	80° C	90° C
A	3.57	1.19	1.19	0.39	0.24	0.18
B	2.86	1.19	4.60	20.10	2.29	0.12
C	0.33	1.19	16.73	4.62	2.62	0.83
D	18.80	0.33	0.18	0.11	0.10	0.08

Figure 17 brings out the interesting fact that the curves do not follow parallel courses, and indicate that the four samples behave quite differently. The  $p_0$  value of slightly degraded Buna-S (Sample A) decreases fairly rapidly as the temperature increases from 40° to 50° C, but above this range the decrease is much slower. The  $p_0$  value of highly degraded, long-stored Buna-S (Sample B) at first decreases with rise in temperature to 50° C; but from 50° to 70° C it increases greatly, and above 70° C it decreases rapidly. The  $p_0$  value of slightly masticated smoked-sheet rubber behaves similarly, except that the maximum  $p_0$  value is reached at 60° C. Finally the  $p_0$  value of highly masticated smoked-sheet rubber (Sample D) decreases from a very high initial value to a very low value at 50° C, and then remains at this very low value without significant change with further rise in temperature. That the increase in the  $p_0$  value of highly degraded Buna-S is attributable to the formation of a network structure which is so characteristic of Buna rubbers is hardly to be doubted. With further increase in temperature the intermolecular forces become insignificant. It is noteworthy that the same phenomenon seems to take place in smoked-sheet rubber. This has not been recognized heretofore, and will have to be verified by further investigation. Another surprising fact is that slightly oxidized Buna-S does not show such a network structure. Further studies are necessary to prove whether these results are true in general. Also a comparison of this physical method for determining the degree of network formation with a purely chemical method would be extremely helpful.

With the method described in the present work a simple rapid means is available for determining the pressure at which plastic flow sets in, and for

determining the temperature to which a plastic material must be raised to bring about flow under a given pressure. This is very important from a practical point of view, for it makes it possible for the works management to give exact instructions for a process already in operation. In addition, the builder of tubing machines and calenders can obtain valuable data for the construction of his machines.

It is especially worthy of note that this so-called yield value is in many cases considerably higher than the pressures which are necessary with plastometers of the Williams and Karrer types. Results obtained with these latter types of plastometers cannot, therefore, be compared with data obtained with an extrusion plastometer.

If the results are summarized in one expression, the following equation is obtained:

$$v_{15} = c \cdot \frac{p^m}{p_0} \cdot t^n \quad (4)$$

The constant  $c$  combines the apparatus constant  $K_A$  and the material constant  $\mu$ , which, in accordance with Bingham, can be regarded as representing the mobility of the plastic mass. Its reciprocal value has been termed stiffness by Bingham.

$$\frac{1}{\mu} = K_A \cdot \frac{p^m}{v_{15} \cdot p_0} \cdot t^n \quad (5)$$

To convert this into the absolute system of measurement,  $p$  and  $p_0$  are recalculated in dynes per sq. cm., i.e., are multiplied by 981, and  $v$  is divided by  $15 \times 60$ , whereby the volume of material extruded is expressed in number of cc. per second.

It is still impossible to offer a formula which can be used directly in a practical way since, in the first place, the value of the apparatus constant is still uncertain and, secondly, any such formula must first of all be reconciled with the formulas derived by other investigators. This subject is reserved for later work.

#### SUMMARY

In the present work, the volume of rubber which flows in unit time from an extrusion plastometer as a function of the pressure and temperature was determined, and the so-called yield value was calculated. This latter value represents the critical shearing stress which must be overcome for true plastic flow to take place. It is shown also that the yield value depends greatly on the temperature and preliminary treatment undergone by the sample.

#### ACKNOWLEDGMENT

The present investigation was carried out in the laboratory of Lehmann and Voss & Co., and the author takes this opportunity to express his appreciation for being allowed to publish the results of the investigation. Gratitude is due also Mr. Günther, Laboratory Assistant, for his part in the experimental work.

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- <sup>2</sup> Behre, *Kautschuk* 8, 169 (1932).
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- <sup>5</sup> Marzetti, *Giorn. chim. ind. applicata*, June 1924, p. 277.
- <sup>6</sup> Behre, Bachmann and Blankenstein, *Kolloid-Z.* 57, 67 (1931).
- <sup>7</sup> Bingham, "Fluidity and Plasticity", New York, 1922.
- <sup>8</sup> In this case a value of  $2 \times 10^{-2}$  for  $c$  is chosen. This value is obtained when the calculated  $p_0$  value is compared with the  $p_0$  value read from the graph.

# IDENTIFICATION OF RAW AND VULCANIZED RUBBER-LIKE POLYMERS. I. "REACTION TIME" IN A MIXTURE OF NITRIC AND SULFURIC ACIDS \*

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## INTRODUCTION AND NATURE OF TEST

In the identification of synthetic rubber, it is a matter of some difficulty to distinguish readily the important type, GR-S, from the equally important natural product. The acid-decomposition test was devised specifically for this purpose, but it has been found to have a wider application.

A recent review<sup>1</sup> of the methods available for the identification and estimation of rubbers refers to the utility of the acid test method developed in these laboratories<sup>2</sup>.

It has been found<sup>2</sup> that the time of reaction of vulcanized butadiene-styrene copolymer with a mixture of nitric and sulfuric acids differs from that of vulcanized natural rubber, and this has been used as a basis of an investigation aimed at developing a technique easily acquired by personnel without scientific training and not needing elaborate laboratory facilities.

*Details of test.*—Thermometer, test-tubes, hot water, a watch, and a supply of acid composed of equal volumes of pure concentrated sulfuric acid and nitric acid (spg. gr. 1.42) are needed, and some simple means of removing acetone-extractable material is advantageous. The mixed acid is poured into a clean dry test-tube to a depth of about one-half an inch. This is placed in water maintained at 70° C, and a small piece of the "rubber", about 1 cu. mm., e.g., a slender thread, or thin flake, previously extracted with or soaked in acetone, is dropped into the acid. The sample will float and the reaction may not be immediately evident. This stage is followed by one in which bubbles of gas appear on the surface of the sample, growing in number until the rubber begins to disintegrate and disperse in the liquid. Complete disintegration is the final stage, in which any carbon black present colors the solution. The first appearance of gas bubbles and the complete disintegration of the sample are difficult to locate accurately in time, but the time that elapses before disintegration starts, i.e., the time from insertion of sample to the first trace of dispersion, can generally be determined with reasonable accuracy, and this is accordingly taken as the "time of reaction". Reactions should be carried out in duplicate in separate tubes. Repetition of the test at 40° C is necessary if the time of reaction at 70° C is less than about 10 seconds.

## REACTION TIMES OF RUBBER IN MIXED ACID

*Results obtained.*—Table I is given to assist the user of the test in identifying an unknown sample, provided it does not contain a mixture of rubbers. It has

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TABLE I  
REACTION TIMES FOR VARIOUS RUBBERS

Type of rubber	Range in seconds for reaction at		No. of compounds tested	
	40° C	70° C		
<i>Unvulcanized rubbers</i>				
Thioplasts { Thiokol-F Thiokol-A	3 2	Too small to determine accurately	1 1	
Natural rubber (smoked sheet)	500-1100		4	1
Polychloroprene (Neoprene-GN)	600	10-13	1	
Butadiene-styrene copolymer (GR-S)	1800	9-15	1	
Polybutadiene (Buna-85)	330-360	9-10	1	
Polyisobutylene	—	1800	1	
<i>Vulcanized rubbers</i>				
Thioplasts { Thiokol-A and Thiokol-F Vulcanized Thiokol latex	0-35 (9-15)	Too small to determine accurately	6	
Vulcaprene	40-50		5	25
Natural rubber, natural rubber reclaim, and vulcanized latex	20-70 (25-60)	0-5		
Polychloroprene and chloroprene copolymers	Neoprene-FR	25-40	2-4	2
	Neoprene-KNR	35-70	5-6	2
	Neoprene-GN	40-60	5-8	2
	Neoprene-I	45-80	5-6	2
	Neoprene-CG	50-80	5	1
	Neoprene-E	50-90	6-9	2
Thiokol-RD	100-250	8-15	2	
	190	4	1	
Butadiene-styrene copolymers { GR-S and Buna-S	630-1200 (630-1140)	10-25	18	
Butadiene-acrylonitrile-copolymers	Perbunan	650-1800	30-60 (35-60)	11
	Hycar OR-15	1000-1300	50-80	5
	Chemigum-I	800-1800	30-120	5
Polybutadienes { Buna-85 and Buna-115	1000-1500	20-35	2	
Isobutylene copolymer (Butyl)	ca. 5000	120-140	2	

been compiled from results obtained on samples of known, but widely differing, composition. Time ranges have been given showing the order of variation to be expected. The range is that for several observers, and extreme values are ignored only when they could not be duplicated. The range in parentheses shows that of a typical single worker. The reaction times for some unvulcanized rubbers have been included also, as these may be met in adhesive tape or as bulk material. Those examined gave off brown fumes of nitrogen peroxide, which were not produced when testing vulcanized samples. The production of brown fumes may therefore provide a suggestion that the sample under test is unvulcanized.

It will be seen that natural rubber, thioplasts and chloroprenes cannot be separated by this test, but the latter two will already have been detected by the odor of sulfur dioxide on burning the thioplast, and by noninflammability and the copper-wire test for chlorine in the case of chloroprene.

Mixtures of rubbers may lead to erroneous conclusions if the reaction is used without confirmatory tests. Ranges of reaction times found for some

mixtures containing  $100 - x$  parts of natural rubber with  $x$  parts of a copolymer are given in Table II. If the components of such binary mixtures are known, it is obviously possible to estimate their ratio to a useful degree of approximation. A simple mixture law is not applicable, for the less reactive rubber component exerts an appreciable protecting influence on the more reactive component.

**Acetone extraction.**—Ester plasticizers and the mixture of complex hydrocarbon products used as extenders react readily with nitric acid, and must be removed if the most information is to be obtained from the tests. If, however, all that is required is to distinguish between a butadiene type of polymer and natural rubber, this removal is unnecessary. The removal is done by extraction with acetone. In the absence of extraction apparatus it will be sufficient, with the small quantities involved, to leave the pieces in acetone in a test-tube overnight and then to wash them in a little fresh acetone. The samples must be dried before test to remove absorbed acetone. The effect of neglecting this extraction is shown by the behavior of a Perbunan compound containing 10 per cent of tricresyl phosphate. The reaction time before extraction was 860 seconds and after extraction 1200–1320 seconds, both at 40° C, the former

TABLE II  
REACTION TIMES FOR MIXTURES OF COPOLYMERS AND NATURAL RUBBER

$x$ parts of copolymer per (100 - $x$ ) parts natural rubber	Range in seconds for "reaction"	
	40° C	70° C
GR-S 0	20-70	0-5
20	240	7-9
33	430	10
50	405	20
80	600-700	12-14
100	650-1200	10-25
Perbunan 0	20-70	0-5
33	500	10-14
67	640	25-37
100	650-1800	30-60

suggesting a butadiene-styrene copolymer, whereas the latter showed that it could be either polybutadiene or a copolymer with acrylonitrile. Repetition of the test at 70° C on another acetone-extracted sample would have confirmed the latter, but at no time was there danger of confusion with natural rubber or chloroprene.

**Effect of fillers.**—Whiting is another compounding ingredient which has been found to interfere with the reaction time, e.g., 37 volumes of whiting in a GR-S vulcanizate containing 100 volumes of GR-S gave a zero reaction time, i.e., instantaneous decomposition, at 70° C, but at 40° C the time recorded was greater than 1800 seconds. Thirty-seven volumes of whiting with 100 volumes of natural rubber gave zero time (instantaneous decomposition) at 70° C, but a normal range (actually 30-40 seconds) at the lower temperature. Such mixtures are unusual, particularly with the butadiene type of synthetics, as carbon-black loading is required for good mechanical properties, and, in any case, are easily recognized.

**Personal factor.**—Comparison of the results obtained by novices shows differences over a moderately wide range, although with slight practice different people obtain results in good agreement with one another. Tests carried out by six persons previously unacquainted with the method gave results from 20

to 105 seconds for a Perbunan mixing, where the standard result was 25–45 seconds, from 95 to 140 seconds for a Neoprene-GN mixing, where the "standard" result was 60 seconds, and from 20 to 42 seconds for a GR-S mixing, where the standard was 18–25 seconds. In practically all cases unskilled operators at first obtain a result greater than the standard value. Practice with one or two samples of known approximate reaction times leads to greater uniformity. It is important to note, however, that, even without practice, the distinction between groups of rubbers is maintained; *i.e.*, GR-S and Perbunan are easily distinguished from natural rubber, Neoprenes, and others.

*Variation of acid composition.*—It has been found that variations in the composition of the acid, especially changes in the proportion of water present, influence the results of the test; these may arise by absorption of water from the atmosphere or by variation in the composition of the original acids, especially the nitric acid. For the 50/50 (by volume) mixture specified for this test, the composition of the acid should be 55.8%  $\text{H}_2\text{SO}_4$ , 31.5%  $\text{HNO}_3$ , and 12.7%  $\text{H}_2\text{O}$ , (all by weight), but it has been found that a variation in water content between 9 and 14 per cent can be tolerated without unduly increasing the variation in the results; the control limits of the mixed acid are, therefore (all by weight),  $\text{H}_2\text{SO}_4$  53–56%,  $\text{HNO}_3$  28–33%,  $\text{H}_2\text{O}$  9–14%. Experiments were made also on the addition of nitrous acid up to 1 per cent; the effects were negligible.

Analysis of the acid is not, in general, necessary, provided that the sulfuric acid used is of 99% concentration or over, and the specific gravity of the nitric acid lies between 1.42 and 1.43 ( $d_4^{25}$ ), *i.e.*, corresponding to 69.8 and 72.2%  $\text{HNO}_3$ . Mixed acid has been found to keep for several months unchanged when stored in the dark in an acid bottle. These bottles have a well-fitting ground glass stopper and a dome, secured also by a ground-glass joint, covering the stopper. Such bottles are frequently recommended for storing ether. Determination of total acid by simple titration enables a check to be kept without recourse to full analysis to show whether the acid mixture has absorbed water.

### SUMMARY

The time taken for the start of disintegration of natural and certain synthetic rubbers in a mixture of nitric and sulfuric acids has been used as a simple and reliable aid in the identification of an unknown rubber. With Perbunan, Buna-S, and Butyl types of rubber, this test seems sufficient to establish identity, but other types, including chloroprenes, thioplasts and natural rubber, require additional data. Indication is also given of ratios of quantities in binary mixtures of known "rubbers". The test does not require a chemical laboratory or special personnel.

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<sup>2</sup> The details in the present paper are part of an investigation carried out by the Research Association of British Rubber Manufacturers, and later incorporated by the Ministry of Supply in a publication (Services Rubber Investigations, Users' Memorandum U-9, Ministry of Supply) which places this method in a general scheme of analysis. Acknowledgment is made to the Ministry of Supply for permission to communicate this paper.

<sup>3</sup> Unpublished observations of A. L. Soden, Research Association of British Rubber Manufacturers.

## DETERMINATION OF TOTAL SULFUR IN RUBBER \*

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In a recent article<sup>1</sup> the author described a rapid method for the determination of total sulfur in small samples of rubber, where the sulfur present did not exceed about 5 mg. This method has proved to be so rapid and convenient that it has appeared desirable to extend its applicability to larger quantities of sulfur. Experiments have shown that this can be done very easily by making a few simple changes in technique.

### REAGENTS

*Nitric Acid-Zinc Oxide-Bromine Mixture.*—Dissolve 20 grams of zinc oxide in 100 cc. of nitric acid and saturate with bromine.

*Acid Mixture for Distillation.*—Place 320 cc. of hydriodic acid (specific gravity 1.70), 320 cc. of hydrochloric acid, and 90 cc. of hypophosphorous acid (50%) in a 1-liter Erlenmeyer flask. Add a few grains of silicon carbide and boil vigorously without cover for 5 minutes. Cool in an ice-bath to room temperature. Keep stoppered in a brown glass-stoppered bottle to avoid oxidation of the hydriodic acid.

*Ammoniacal Cadmium Chloride Solution.*—Dissolve 20 grams of cadmium chloride dihydrate in water. Add 200 cc. of ammonium hydroxide and 150 cc. of 1% starch solution and dilute to 2 liters.

*Nitrogen.*—Commercial "prepurified" lecture bottle tank nitrogen.

*Standard Potassium Iodate Solution (0.1 N).*—Recrystallize C.P. potassium iodate from water twice and dry at 180° C to constant weight. Weigh 7.134 grams of the pure potassium iodate and dissolve in water. Add 2 grams of sodium hydroxide and then 50 grams of potassium iodide (free from potassium iodate). After complete solution of all salts, adjust to room temperature and dilute to 2 liters in a volumetric flask.

*Standard Sodium Thiosulfate Solution (0.1 N).*—Dissolve about 50 grams of sodium thiosulfate pentahydrate in 2 liters of freshly boiled and cooled distilled water. Store in a clean Pyrex bottle. To standardize this solution, pipet 25 cc. of the standard potassium iodate solution into a 300-cc. Erlenmeyer flask. Add 150 cc. of water and 20 cc. of hydrochloric acid and then titrate with the thiosulfate solution. As the end point is approached add 2 cc. of 1% starch solution and titrate carefully until the solution is colorless.

*Starch Solution.*—Add a cold aqueous suspension of 10 grams of soluble starch to 1 liter of boiling water. Cool to room temperature and store in a clean bottle.

### PROCEDURE

Dissolve 0.5 gram of the rubber sample (containing 5 to 100 mg. of sulfur) in 10 cc. of nitric acid-zinc oxide-bromine mixture and 15 cc. of fuming

\* Reprinted from *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 17, No. 5, pages 298-299, May 1945.

nitric acid in a 200-cc. Erlenmeyer flask as described<sup>1</sup>. After destruction of the organic matter and conversion of zinc nitrate to oxide, add 10 cc. of hydrochloric acid and boil down to near dryness to expel all oxides of nitrogen. Repeat if necessary. Add 35 cc. of hydriodic acid mixture, and immediately cap with the distillation head. Place on a hot plate with surface temperature of 170° to 200° C, with the condenser tube dipping to within about 0.5 cm. from the bottom of a 300-cc. tall-form beaker containing 150 cc. of ammoniacal cadmium chloride solution. Pass a slow stream of pure nitrogen through the solution by way of the capillary pressure regulator tube. Adjust the flow of nitrogen so that it escapes from the receiver solution at a rate of about 3 bubbles per second. (The rate of flow is not critical, providing it is not so fast as to prevent complete absorption of the hydrogen sulfide by the receiver solution or so slow as to permit the ammoniacal solution to be sucked back into the acid solution.)

Heat the acid solution until fumes of ammonium chloride begin to appear over the ammoniacal solution, and then continue for 10 minutes longer. Remove the distillate flask and detach the distillation head at once. Transfer the traces of cadmium sulfide from the condenser tube of the distillation head to the ammoniacal solution with the aid of a policeman and wash bottle.

Buret or pipet enough standard 0.1 N potassium iodate solution to provide a 5- to 25-cc. excess over that required for oxidation of the sulfide, to a 500-cc. iodine flask. Add 25 cc. of hydrochloric acid to the iodate in the flask and wash down the sides with water. Immediately pour the ammoniacal solution into the flask and transfer all the sulfide with the aid of a policeman and wash bottle. (If the starch-iodine color disappears, showing that too little iodate has been used, immediately add more iodate from a buret to provide about a 5-cc. excess.) Immediately stopper and shake vigorously to entrap any sulfide in the atmosphere in the flask. Titrate with standard 0.1 N sodium thiosulfate solution. Run a blank through the whole procedure, using 5 cc. of potassium iodate solution for the oxidation of the sulfide.

If (cc. of  $\text{KIO}_3$  - cc. of  $\text{Na}_2\text{S}_2\text{O}_3 \times \text{KIO}_3$  factor) =  $A$  and (cc. of  $\text{KIO}_3$  for blank - cc.  $\text{Na}_2\text{S}_2\text{O}_3$  for blank  $\times \text{KIO}_3$  factor) =  $B$ , then:

$$\frac{0.1603 (A - B)}{\text{sample weight in grams}} = \text{per cent sulfur}$$

#### DISCUSSION

In the method above the distillation is performed at a much lower temperature than that previously used, and gaseous nitrogen is used to sweep the hydrogen sulfide out of the flask. This procedure eliminates the danger of loss of sulfide caused by incomplete absorption in ammoniacal cadmium chloride solution, when large quantities of hydrogen sulfide are suddenly distilled over.

The method cannot be used for samples which contain barium (and presumably lead and calcium) because the insoluble sulfate is but slowly decomposed.

The iodometric titration of large amounts of hydrogen sulfide suggested in the previous publication is not very sound, since the loss of a certain amount of iodine can hardly be avoided. Attempts to titrate the sulfide by addition of a measured excess of a standard Wijs solution (iodine monochloride in glacial acetic acid), followed by back-titration of the excess iodine, failed because high results were obtained, due presumably to partial oxidation of the sulfide to sulfate.

When large amounts of sulfide are titrated iodometrically, the precipitated sulfur may occlude appreciable amounts of iodine. This error can be eliminated by dissolving the sulfur in carbon disulfide, but a better procedure is to keep the sulfur colloiddally dispersed with the aid of starch.

It is essential that nitrogen acids be completely expelled before the distillation with hydriodic acid, otherwise sulfide will be oxidized to sulfur during the distillation, and unstable end points will be encountered in the titrations with thiosulfate.

#### APPLICATION OF THE METHOD TO INORGANIC ANALYSIS

The new method for the determination of sulfate<sup>1</sup> has proved very useful in the analysis of sulfur in chemicals and alloys where the usual methods fail. Following is an outline of the method used in these laboratories for the determination of 0.0005 to 0.05% sulfur in molybdenum permalloy, *i.e.*, 79% nickel, 17% iron, and 4% molybdenum.

Dissolve 10 grams of the metal in 80 cc. of aqua regia. Evaporate to moist dryness to expel most of the excess acid. Add 35 cc. of hydrochloric acid and heat to dissolve all soluble salts. Add 25 cc. of formic acid and heat to destroy the nitric acid. Transfer the solution to a 200-cc. flask and reduce the volume to 50–60 cc. by boiling. Add 35 cc. of acid mixture and perform the distillation as directed in the procedure above, doubling the time of distillation (and also the concentration of ammonium hydroxide in the receiver) to assure complete expulsion of the hydrogen sulfide. Titrate as directed<sup>1</sup>.

#### EXPERIMENTAL

A standard solution of potassium sulfate was prepared by dissolving 27.18 grams of the pure dry salt in water and diluting to 1 liter in a volumetric flask. Aliquot portions of the solution were evaporated to dryness in 200-cc. Erlenmeyer flasks. Hydriodic acid mixture was added, and the samples were then analyzed for sulfur as directed in the procedure. In some instances, 10 cc. of nitric acid-zinc oxide-bromine mixture were added to the sulfate sample, and the nitric acid and bromine were expelled before distillation and titration (see Table I).

TABLE I  
DETERMINATION OF SULFUR IN POTASSIUM SULFATE BY THE PROPOSED METHOD

No.	Sulfur present (mg.)	KIO <sub>3</sub> used (cc.)	Sulfur found (mg.)	Error (mg.)
1	5.0	5	5.1	+0.1
2	5.0	5	5.0	±0.0
3 <sup>a</sup>	5.0	25	5.1	+0.1
4	10.0	50	10.0	±0.0
5	10.0	10	10.0	±0.0
6 <sup>b</sup>	10.0	10	9.9	-0.1
7	10.0	10	10.0	±0.0
8 <sup>a</sup>	25.0	25	25.0	±0.0
9	50.0	50	50.0	±0.0
10 <sup>a</sup>	50.0	50	49.8	-0.2
11	100.0	75	100.2	+0.2
12 <sup>b</sup>	100.0	75	99.9	-0.1
13 <sup>a</sup>	100.0	75	99.8	-0.2

<sup>a</sup> HNO<sub>3</sub>-ZnO-Br mixture used.

<sup>b</sup> Distillate containing CdS cooled to 10° C before titration.

## SUMMARY

The range of the hydriodic acid reduction-iodometric titration method for the determination of sulfur in semimicrosamples of rubber has been extended to provide for the analysis of macrosamples containing as much as 100 mg. of sulfur.

## ACKNOWLEDGEMENT

The author is indebted to B. L. Clarke of these laboratories, who read the manuscript.

## REFERENCE

- <sup>1</sup> Luke, *Ind. Eng. Chem., Anal. Ed.* **15**, 602 (1943); *RUBBER CHEM. TECH.* **17**, 227 (1944).

## HIGH-TEMPERATURE OVEN AGING OF OIL-RESISTING SYNTHETIC RUBBER COMPOUNDS \*

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### INTRODUCTION

Synthetic rubber vulcanizates of all types commercially available today become stiffer when exposed to elevated temperatures in an air oven; that is, the modulus increases and the elongation is reduced. This change is thought to be due principally to a cyclization of the rubber, which apparently requires the presence of oxygen. In addition, some stiffening may be due to the loss of volatile plasticizers during the heating. Early in the program of development of stocks to withstand 300° F oven tests, it was discovered that the results obtained were quite erratic, and depended to a considerable extent on the volume of air (or the concentration of oxygen) to which the samples were subjected. It was the object of the work undertaken by the Subsection to study the effects of variables in the oven-testing procedure and to devise, if possible, a reproducible laboratory technique for conducting air oven tests at 300° F or at other temperatures higher than those normally used in rubber testing. The work done was confined to vulcanizates of the SB type<sup>1</sup>.

### PROCEDURE

The work consisted of three parts, the first being a study of widely different methods of exposures for the purpose of determining the factors influencing deterioration, the second a study of the duplicability of a refinement of one of the methods used in the first part, and the third a study of time and temperature relations, using the latter method.

Three compounds, designated A, B, and C, were chosen for testing, and the recipes are given in Table I. Compound A is a heat-resisting type containing a volatile plasticizer, compound B is similar except that the plasticizer is omitted, and compound C is a conventional stock not designed for heat resistance. Service experience has shown that stocks similar to A and B perform more satisfactorily in high-temperature service than stocks similar to C.

Samples of the three compounds were prepared by The Ohio Rubber Co. In order that no variables due to the use of different dies or cutting methods would be introduced, the dumbbells were cut by The Ohio Rubber Company and distributed by them to the cooperating laboratories. This procedure was followed in all three studies.

\* Reprinted from the *ASTM Bulletin*, No. 132, pages 33-37, January 1945. The authors constitute a Subsection of Section IV on the Classification and Specifications of Rubber Compounds of Technical Committee A of A.S.T.M. Committee D-11 on Rubber and Rubberlike Materials. This paper is a progress report. The addresses of the authors are as follow. G. D. McCarthy, Chrysler Corporation, Detroit, Michigan; A. E. Juve, The B. F. Goodrich Co., Akron, Ohio; H. Boxser, Acadia Synthetic Division, Western Felt Works, Chicago, Illinois; M. Sanger, The General Tire and Rubber Co., Akron, Ohio; S. R. Doner, Manhattan Rubber Division, Raybestos-Manhattan, Inc., Passaic, New Jersey; E. N. Cunningham, Stanco Distributors, Inc., New York, N. Y.; J. F. McWhorter, Ohio Rubber Co., Willoughby, Ohio; R. H. Crossley, Xylos Rubber Co., Akron, Ohio.

TABLE I  
THREE COMPOUNDS CHOSEN FOR TESTING

	Compound A	Compound B	Compound C
Hycar OR-15	50	50	50
Perbunan	50	50	50
Stearic acid	0.5	0.5	0.5
AgeRite resin D	5	5	5
Zinc oxide (No. 72)	5	5	5
SRF black (Gastex)	70	70	70
Sulfur	...	...	1.5
Tuads	3	3	...
Captax	1.5	1.5	1.5
Plasticizer-SC	15	...	15
	200	185	198.5

Cured 25 min. at 307° F

#### PART I.—STUDY OF METHODS OF EXPOSURE

Each laboratory of the four in this study ran the following tests:

1. Original properties—tensile strength, ultimate elongation, modulus, and durometer hardness.
2. Properties after 70 hrs. at 300° F in mercury or a low melting alloy.
3. Properties after 70 hrs. at 300° F in circulating nitrogen.
4. Properties after 70 hrs. at 300° F in a bottle of 250 cc. capacity.
5. Properties after 70 hrs. at 300° F in a bottle of 375 cc. capacity.
6. Properties after 70 hrs. at 300° F in a bottle of 500 cc. capacity.
7. Properties after 70 hrs. at 300° F in circulating air oven with intake port closed.
8. Properties after 70 hrs. at 300° F with intake port open.

In addition, the heat loss during each test was measured and a 180-degree bend test was made.

#### PART II.—STUDY OF DUPLICABILITY OF REFINEMENT ON BOTTLE TEST

The bottle test used in Part I was modified in the following respects:

1. Containers for samples were test-tubes 38 by 300 mm.
2. Test-tubes were heated by immersion in an oil bath maintained at 300° F.
3. Test-tubes were stoppered with an unvented cork.
4. Samples were suspended as near the bottom of the test-tube as possible.

The following tests were run by six coöperating laboratories:

1. Original tensile strength, ultimate elongation, and durometer hardness.
2. Same properties and a 180-degree bend test after 70 hrs. at 300° F.
  - (a) Three successive times, using one specimen per test-tube.
  - (b) Three successive times, using three specimens per test-tube.

#### PART III.—STUDY OF TIME AND TEMPERATURE RELATIONS

Using the same technique as above and with three specimens per test-tube, a series of tests was run on compounds A and B by seven coöperating laboratories as follows:

- 1, 2, 4, 8, 16, 32, 48, and 70 hrs. at 300° F
- 8, 16, 32, 64, and 128 hrs. at 250° F

Parts I, II, and III were run at different times, and a different lot of test-specimens was supplied for each part. Although the compositions of the stocks were identical in all three parts, slight differences in materials and processing may have occurred which caused slight variations in the original properties.

### RESULTS

The results obtained in the three parts of this study are given in Tables II to V and Figures 1 to 5.

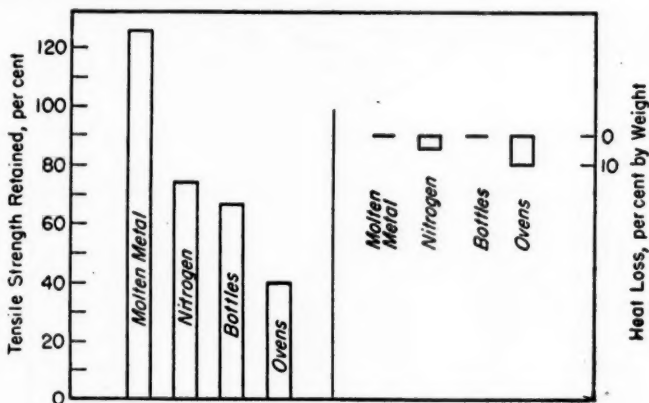


Fig. 1.—Heat aging tests, 70 hrs. at 300° F—compound A.

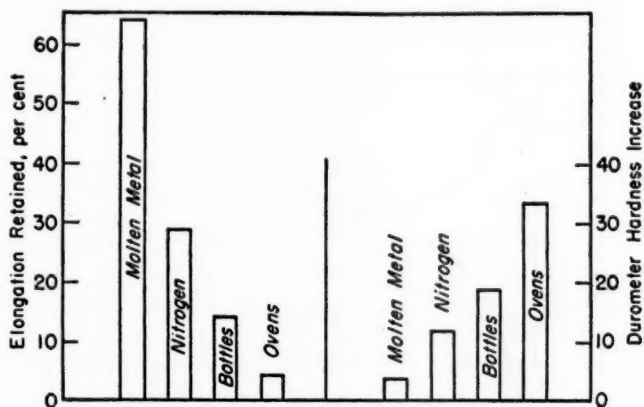


Fig. 2.—Heat aging tests, 70 hrs. at 300° F—compound A.

The percentage deviation as used in this report is the average deviation expressed as a percentage of the average value for the property being considered.

### DISCUSSION

From the data in Table II and in Figures 1 and 2, it will be seen that the oven tests were too severe, as they nearly completely deteriorated all compounds without consistently distinguishing between the heat-resisting and non-heat-

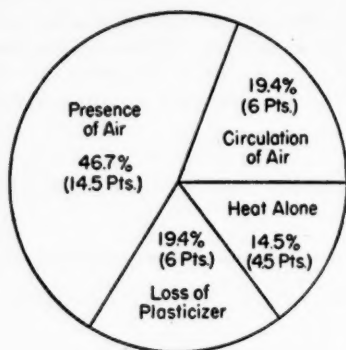


Fig. 3.—Effect of various factors on hardening of compounds A and C.

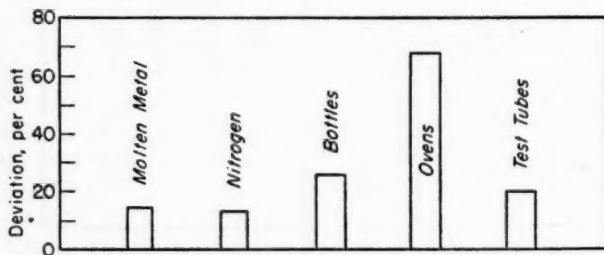


Fig. 4.—Deviation in elongation tests. Averages for compounds A, B, and C tested by all laboratories under various conditions of exposure.

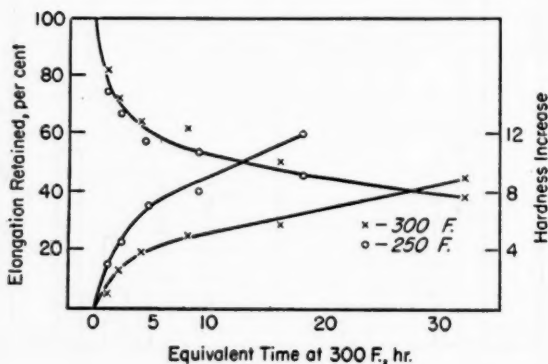


Fig. 5.—Effect of temperature—compound A.

resisting compounds. Moreover, the deviation between laboratories, particularly in elongation, was found to be extremely high.

On the other hand, the test in molten metal was not severe enough to differentiate between the compounds. The test in nitrogen, although more severe, was still not severe enough to differentiate between the compounds.

The bottle tests, although nearly as severe as the oven tests, were, nevertheless, more duplicable, and differentiated in every case between the heat-resist-



TABLE II—Continued

	Compound A			Compound B			Compound C		
	Properties	Change	Deviation (per cent)	Properties	Change	Deviation (per cent)	Properties	Change	Deviation (per cent)
Tensile strength Elongation Durometer hardness Weight change (per cent) 180-degree bend	1120	-33%	28.6	70 Hr. AT 300° F IN 500-CC. BOTTLES			970	-58%	10.3
	120	-86%	27.7	1221	-42%	15.2	45	-92%	7.3
	71	+18	....	86	-87.5%	18.7	79	+20	....
	-0.9	....	....	83	+18.7	....	+1.1	....	....
	OK	....	....	-0.35	....	....	NG	....	....
Tensile strength Elongation Durometer hardness Weight change (per cent) 180-degree bend	70 Hr. AT 300° F IN CIRCULATING AIR OVEN—LIMITED AIR			OK	....	....	603	-74%	11.4
	800	-53%	15.8	757	-65%	22.3	15	-97%	44.7
	40	-95%	65.0	32	-94%	90.8	87	+27	....
	84	+32	....	86	+19.7	....	-9.7	....	....
	-9.9	....	....	-4.2	....	....	NG	....	....
Tensile strength Elongation Durometer hardness Weight change (per cent) 180-degree bend	70 Hr. AT 300° F IN CIRCULATING AIR OVEN—UNLIMITED AIR			NG	....	....	587	-75%	25.8
	560	-67%	18.5	668	-68.7%	18.1	18	-97%	61.0
	30	-96%	50.0	35	-94%	94.3	91	+31	....
	87	+35	....	88	+23	....	-9.3	....	....
	-10.6	....	....	-4.1	....	....	NG	....	....
	NG	....	....	NG	....	....			

TABLE III  
AVERAGES OF TESTS BY ALL LABORATORIES—PART II

	Compound A			Compound B			Compound C		
	Property	Change	Deviation (per cent)	Property	Change	Deviation (per cent)	Property	Change	Deviation (per cent)
Tensile strength Elongation Durometer hardness	1850	....	3.4	ORIGINAL	....	2.8	2219	....	3.3
	825	....	3.8	2138	....	3.8	534	....	3.2
	53	....	5.7	637	....	4.7	58	....	5.2
70 HRS. AT 300° F.—TEST TUBE METHOD—ONE STRIP PER TEST-TUBE									
Tensile strength	1302	-29%	16.0	1553	-26.0%	7.7	842	-62%	7.7
Elongation	102	-88%	9.2	95	-85%	11.0	41	-92%	29.0
Durometer hardness	73	+20	....	79	+12	....	79	+20	....
180-degree bend	OK	....	....	OK	....	....	NG	....	....
70 HRS. AT 300° F.—TEST TUBE METHOD—THREE STRIPS PER TEST-TUBE									
Tensile strength	1107	-40%	10.4	1431	-32%	6.5	789	-64%	9.0
Elongation	97	-88%	11.0	107	-82%	19.7	47	-92%	43.0
Durometer hardness	72	+19	....	78	+11	....	77	+18	....
180-degree bend	OK	....	....	OK	....	....	NG	....	....

TABLE IV  
AVERAGES OF TESTS BY ALL LABORATORIES—PART III

	Compound A			Compound B		
	Property	Change	Deviation (per cent)	Property	Change	Deviation (per cent)
Tensile strength Elongation Durometer hardness	2039	.....	4.4	2576	.....	1.5
	618	.....	5.0	522	.....	4.8
	54	.....	.....	64.3	.....	.....
Tensile strength Elongation Durometer hardness	2116	1 Hr. at 300° F	6.9	2823	+ 9.5%	3.0
	507	+ 3.7%	6.3	449	- 13.87%	4.0
	55	+ 1	.....	66.1	+ 1.8	.....
Tensile strength Elongation Durometer hardness	2118	2 Hrs. at 300° F	3.0	2788	+ 8.0%	2.6
	447	+ 3.9%	4.7	403	- 22.7%	6.2
	56.6	+ 2.6	.....	66.5	+ 2.2	.....
Tensile strength Elongation Durometer hardness	2229	4 Hrs. at 300° F	4.4	3001	+ 17.0%	4.6
	396	+ 9.3%	9.1	357	- 31.5%	10.9
	57.8	+ 3.8	.....	67.5	+ 3.2	.....
Tensile strength Elongation Durometer hardness	2208	8 Hrs. at 300° F	5.3	2973	+ 15.4%	7.9
	382	+ 8.3%	8.1	340	- 34.8%	7.8
	59	- 38.2%	.....	69	+ 4.7	.....
Tensile strength Elongation Durometer hardness	2201	16 Hrs. at 300° F	8.9	2781	+ 8%	6.6
	311	+ 7.9%	7.7	289	- 44.6%	8.4
	59.8	- 49.7%	.....	70	+ 5.7	.....
Tensile strength Elongation Durometer hardness	1748	32 Hrs. at 300° F	3.3	2078	- 19.4%	14.4
	238	- 15.5%	5.0	194	- 62.8%	8.7
	63	- 61.5%	.....	71	+ 6.7	.....

TABLE IV—Continued

	Compound A			Compound B		
	Property	Change	Deviation (per cent)	Property	Change	Deviation (per cent)
Tensile strength Elongation Durometer hardness	1510	48 Hrs. AT 300° F	15.3	1865	-27.6%	15.4
	175	-26%	7.1	165	-68.4%	12.1
	64	-71.7%	....	73	+ 8.7	....
Tensile strength Elongation Durometer hardness	1034	70 Hrs. AT 300° F	11.1	1398	-45.7%	14.7
	118	-49.2%	11.8	108	-79.3%	9.3
	69.5	-80.9%	....	76	+11.7	....
Tensile strength Elongation Durometer hardness	2226	8 Hrs. AT 250° F	6.2	2840	+10%	4.8
	459	+ 9.2%	7.2	426	-18.3%	6.8
	57	-25.7%	....	67.3	+ 3	....
Tensile strength Elongation Durometer hardness	2163	16 Hrs. AT 250° F	6.7	3053	+18.5%	5.8
	411	+ 6.1%	9.0	400	-23.3%	11.1
	58.5	-33.5%	....	68.5	+ 4.2	....
Tensile strength Elongation Durometer hardness	2166	32 Hrs. AT 250° F	7.9	3012	+17%	4.7
	352	+ 6.2%	8.1	326	-37.5%	9.1
	61	-43%	....	69.3	+ 5	....
Tensile strength Elongation Durometer hardness	2361	64 Hrs. AT 250° F	9.1	3058	+18.8%	5.6
	330	+15.8%	9.2	293	-43.8%	6.5
	62	-46.5%	....	72	+ 7.7	....
Tensile strength Elongation Durometer hardness	2390	128 Hrs. AT 250° F	8.0	3111	+21%	6.1
	283	+17.2%	10.1	263	-49.6%	6.8
	66	-56.2%	....	73	+ 8.7	....

TABLE V

	Compound A		Compound C	
	Percentage elongation retained	Bend test	Percentage elongation retained	Bend test
Molten metal	64	OK	58	OK
Nitrogen	29	OK	33	OK
250-cc. bottle	12	OK	6	NG
375-cc. bottle	17	OK	10	NG
500-cc. bottle	14	OK	8	NG
Oven, limited air	5	NG	3	NG
Oven, unlimited air	4	NG	3	NG

ing and non-heat-resisting compounds, particularly in elongation retention and the 180-degree bend test (see Table V).

Figure 3 shows a breakdown of the change in durometer hardness of compound A attributable to various changes in the conditions of exposure. These data, as well as the tensile and elongation data, indicate that the changes in elongation and hardness are approximately proportional to the air (or oxygen) available during the test. In both the molten metal and circulating nitrogen tests, all oxygen could not be excluded, since it is virtually impossible to remove traces of oxygen dissolved or occluded in the specimens. Also, commercial nitrogen contains traces of oxygen. There was little difference between the results obtained in the static air tests in the three sizes of bottles, which indicates that variation in the oxygen supply over this range has little effect. The difference between the static air tests and the circulating air oven tests is probably due both to the greater volume of available oxygen and to the loss in plasticizer. Appreciable loss of plasticizer occurred only in those tests in which a circulating medium was used.

It is probable that all the changes taking place, exclusive of those due to plasticizer loss, are the result of heating in the presence of oxygen.

The factors which must be most carefully controlled are the availability of oxygen and the temperature. Since it is extremely difficult to control the temperature in different parts of a circulating air oven within narrow limits and to control the volume of air per unit area of sample exposed, it seemed that the static air test using test-tubes immersed in an oil bath would have the best possibility of fulfilling both of these requirements.

The data on these tests given in Table III indicate excellent reproducibility and a measurable distinction between the heat-resisting and non-heat-resisting compounds. It was felt that this distinction was not so sharp as it should be, due to the severity of the deterioration. The differences between the use of one strip per test-tube and three strips were slight and not sufficient to warrant this restriction in testing capacity. A comparison of the deviation between laboratories for the elongation deterioration after various conditions of exposure is shown in Figure 4.

The tests run in Part III were for the purpose of determining whether the temperature coefficient of aging is the same as that reported for GR-S<sup>2</sup>, and whether a test at lower temperature carried to the same degree of deterioration would be more duplicable than one run at 300° F.

In Figure 5 are shown the elongation and durometer hardness change for compound A at 250° F and at 300° F. The times at 250° F were adjusted to equivalent times at 300° F, on the assumption that the rate of change of properties on aging were doubled for an 18° F increase in aging temperature.

It will be noted that the elongation changes are in accord with this assumption, but that the hardness changes are not. For equivalent times on the above basis, the hardness increase is greater at 250° F than at 300° F. The temperature required for doubling the rate of hardness increase is 42° F.

In Figure 6 the changes in elongation, tensile strength, and durometer

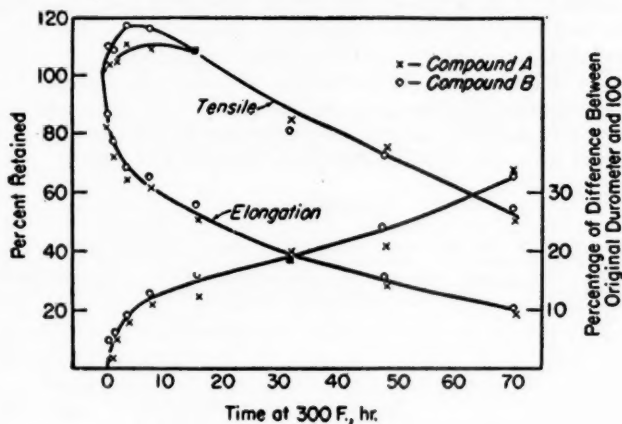


FIG. 6.—Aging of compounds A and B at 300° F.

hardness for compounds A and B with time at 300° F are shown. Except for a slight difference in tensile strength in the first 15 hours of exposure, the curves for compounds A and B are identical. Since the difference between these compounds is only in their plasticizer content, it is evident that, in terms of percentage of properties retained after aging, plasticizer makes no difference. It is also evident that the rate of deterioration at 300° F is quite rapid, and the degree of deterioration after 70 hours at 300° F very great.

A comparison of the deviations between laboratories in tensile and elongation retention after exposure for several approximately equivalent periods at 300° and 250° F is shown in Table VI. Excellent duplicability was obtained

TABLE VI  
REPRODUCIBILITY OF TESTS—300° F Versus 250° F

Hours at 250° F	Deviation between laboratories (per cent)		Hours at 300° F	Deviation between laboratories (per cent)	
	Tensile	Elongation		Tensile	Elongation
8	6.2	7.2	1	6.9	6.3
16	6.7	9.0	2	3.0	4.7
32	7.9	8.1	4	4.4	9.1
64	9.1	9.2	8	5.3	8.1
128	8.0	10.1	16	8.9	7.7

at both temperatures. It is probable that a similar test, with the conventional circulating air ovens, would have shown an appreciable difference in reproducibility in favor of the lower temperature.

#### CONCLUSIONS

An investigation of the effect of varying conditions of high-temperature exposure has shown that, at a constant temperature, the supply of oxygen is the

principal factor which causes stiffening of the vulcanizates. The loss of volatile plasticizers, when present, also contributes to the stiffening.

The test-tube technique, developed in the course of this investigation, in which dumbbell samples are suspended in stoppered test-tubes (38 by 300-mm.) heated by immersion in an oil bath, appears to give results which are considerably more duplicable than those obtained by the usual aging in circulating air ovens. The test-tube technique also gives somewhat better differentiation between good-heat aging and poor-heat aging compounds.

The rate of deterioration as measured by elongation change is doubled for an 18° F increase in the exposure temperature. As measured by hardness change the rate is doubled by an increase of 42° F. Tests run at 250° F by this method are no more reproducible than those run at 300° F.

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- <sup>2</sup> Harrison and Cole, "Time-temperature relations in oven-aging of GR-S", *Ind. Eng. Chem.* **36**, 702 (1944); Juve and Garvey, "The effect of time and temperature of cure on GR-S tread stocks", *Ind. Eng. Chem.* **36**, 212 (1944).

## A SOLUTION METHOD FOR THE COMPOUNDING OF GOLDENROD RUBBER \*

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In hevea, kok-sagyz, guayule, and the stems of *cryptostegia*, rubber is present as latex in the laticiferous duct systems of the plants. These latex rubbers can be isolated in the form of relatively hard, nervy, nonsticky materials, in which compounding ingredients are readily dispersed by milling.

In goldenrod and in the leaves of *cryptostegia*, rubber occurs in the form of isolated globules floating free among the plastids in the protoplasm of the palisade and spongy parenchyma cells; occasionally three to five globules can be found in a single cell, but they usually occur singly, and average about 2 microns in diameter. Whether the rubber in these globules is in a solid or liquid state has not been determined, but it obviously cannot be isolated by bleeding. It is best obtained by solvent extraction of the dried, ground leaf-material, and even after practically complete deresinification, the rubber is soft and sticky and of too low plasticity for milling.

Recovery and utilization of rubber from goldenrod have been studied experimentally and on a pilot-plant scale at the Southern Regional Research Laboratory as part of the Emergency Rubber Project<sup>1</sup>.

The raw material used in this investigation was the dried, ground plant-material from selected strains of a variety of goldenrod (*Solidago leavenworthii*), from which the rubber was removed by solvent extraction with benzene after removal of resins with acetone. On complete removal of benzene, the raw rubber was so soft and sticky that its handling and compounding on either hot or cold mixing rolls were extremely difficult. Vulcanizates prepared by the addition of chemicals on mixing rolls in the conventional manner were of low tensile strength, and they contained scorched spots and air bubbles, indicating poor dispersion and poor mould flow.

Since the rubber was initially obtained in benzene solution, an investigation was undertaken to determine whether the dispersion could be improved by adding a part of the compounding chemicals directly to the benzene solution. The advantages of this procedure were twofold: (1) better dispersion of some of the chemicals, and (2) considerable stiffening or "precuriing" of the stock by heating the partially compounded rubber for a short time at approximately 200° F, after removal of the benzene.

This precuriing permitted much better working of the rubber on the mixing rolls for the subsequent addition and dispersion of the remainder of the chemicals for complete compounding. A number of vulcanizates prepared by this solution method of compounding gave increases in tensile strength of about 2000 lbs. per sq. in. above those prepared from soft stock by the conventional milling method.

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A more detailed study of precuring conditions showed that, when the temperature was increased to 250°–280° F, the use of smaller portions of compounding chemicals resulted in a stock suitable for milling and complete compounding, and gave vulcanizates of good quality. This finding was important because, in the preparation of a semicompounded material for possible commercial use, it would permit considerably more latitude in the choice of the final compounding formula.

### EXPERIMENTAL WORK

*Laboratory Conventional Milling.*—In an investigation of the quality of soft rubber extracted from goldenrod, chemicals were added on mixing rolls in the conventional manner. The tentative standard formula suggested by the Crude Rubber Committee<sup>2</sup> for the evaluation of raw rubber was found to be unsatisfactory. By increasing the stearic acid from 0.5 part to 5 parts and the accelerator from 0.5 to 1.0 part, it was possible to prepare vulcanizates in reasonable curing periods. This modified formula is shown as Formula No. 1.

FORMULA No. 1

	Parts
Rubber	100.
Mercaptobenzothiazole	1.0
Stearic acid	5.0
Sulfur	3.5
Zinc oxide	6.0

By curing for 60 minutes at 260° F and 2000 lbs. per sq. in. pressure, vulcanizates that had good elongations were prepared, but tensile strength measurements of a large number of samples were erratic and low, fluctuating between 300 and 1300 lbs. per sq. in. These vulcanizates contained scorched spots, which indicated poor dispersion of compounding chemicals. In addition, this raw stock exhibited poor mould flow, resulting in porosity due to trapping of air. These preliminary experiments show that vulcanizates of good quality cannot be prepared from soft goldenrod rubber by the conventional milling method.

*Solution compounding.*—A series of experiments was made in which several combinations of compounding chemicals, including all the sulfur and most of the accelerator in solution, were added to 50–100 gram samples of rubber dissolved in benzene in glass containers. Steam baths were used to distill the benzene from these mixtures of rubber and chemicals, and vacuum was applied to lower the distillation temperature and assure complete removal of the benzene. These mixtures were heated for additional short periods to set up or precure these stocks. The remainder of the chemicals were added on the mixing rolls in the conventional manner. The completely compounded stocks were vulcanized in strips 6 inches long, 1.75 inches wide, and 0.06 inch thick, by curing at 260° F and 2000 lbs. per sq. in. on the mould.

In the first experiment on solution-compounding, the chemicals were added as shown in Table I, Formula No. 2. The partially compounded rubber stock, after removal of benzene, was heated on the steam bath for 90 minutes at about 200° F. The rubber at this point appeared to be uniform, but it was very soft and sticky. By heating in an oven at 260° F for another 30 minutes, it was possible to toughen or precure the material sufficiently to permit handling on the rolls. Vulcanized samples prepared from this stock were porous, and contained scorched spots.

TABLE I

CHEMICALS USED IN THE FIRST SERIES OF EXPERIMENTS ON SOLUTION COMPOUNDING

Formula No.	2	3	4	
Rubber	100.	100.	100.	} Added in solution
Flectol-H	0.5	0.5	0.5	
Sulfur	3.5	3.5	3.5	
Stearic acid	5.0	...	...	
Mercaptobenzothiazole	1.0	1.0	...	
Diphenylguanidine	0.3	0.3	0.3	} Added on rolls
Zinc mercaptobenzothiazole	...	...	1.2	
Zinc Stearate	...	5.5	...	
Zinc oxide	6.0	5.5	5.8	
Carbon black (Statex)	50.0	50.0	50.0	
Diphenylguanidine	0.5	0.5	0.5	

Note: Figures refer to parts by weight.

Samples containing chemicals, as shown in Table I, Formulas No. 3 and No. 4, also appeared uniform after removal of benzene, and in addition had toughened markedly after an additional heating period at 200° F of only 30 minutes. The handling of the stock on the mill was, therefore, greatly facilitated. No difficulty was experienced with the rubber sticking to the rolls during the milling procedure, and the material was sufficiently nerry to permit maintenance of a tight bank, which made possible better dispersion. The resulting vulcanizates had maximum average tensile strengths of 2590 and 2535 lbs. per sq. in., and ultimate elongations of 525 and 600 per cent, at these particular cures respectively, as shown in Table II. In addition, samples prepared without carbon were nonporous and free of bubbles.

TABLE II

TENSILE STRENGTHS AND ELONGATIONS OF VULCANIZATES

Formula No.	Curing time at 260° F (min.)	Modulus of elasticity at elongation of		Maximum tensile strength (lbs. per sq. in.)	Ultimate Elongation (%)
		300%	500%		
3	10	870	2035	2390	575
	20	1245	2430	2590	525
	30	1410	....	2390	475
	40	1410	....	2360	450
	60	1475	....	2295	425
4	10	335	1065	1870	675
	20	565	1530	2340	675
	30	700	1800	2470	650
	40	800	2000	2535	600
	60	1000	2370	2535	550
6	10	....	....	2655	500
	20	1520	3085	3125	510
	30	....	....	3095	475
	40	....	....	3000	435

Owing to the high temperature and longer heating time necessary for pre-curing the stock compounded with Formula No. 2, it appeared that either Formula No. 3 or No. 4 was more promising, where zinc had been used in the soluble form in the precuring step to assure good dispersion of the accelerator activator. Formulas No. 3 and No. 4 are modifications of the original Formula No. 2, in which the stearic acid was stoichiometrically replaced by zinc stearate,

and the mercaptobenzothiazole was stoichiometrically replaced by the zinc salt of this acid. These preliminary experiments show that solution compounding is a highly advantageous step in the preparation of good vulcanizates from goldenrod rubber.

The solution method was also tried on a sample of hevea smoked sheet. The sample of rubber was dissolved in benzene, the chemicals were added in solution, and the benzene was removed as described previously in the laboratory investigation. The only significant change in the formula recommended for hevea by the Crude Rubber Committee was the use of 0.55 part of zinc stearate in place of 0.5 part of stearic acid, as shown in Formula No. 5 below:

FORMULA No. 5

	Parts	Remarks
Rubber	100.	Added in solution
Mercaptobenzothiazole	0.5	Added in solution
Zinc stearate	0.55	Added in solution
Sulfur	3.5	Added in solution
Zinc oxide	5.95	Added on rolls

Vulcanizates from this material, cured for 80 minutes at 260° F, had an average tensile strength of 3200 lbs. per sq. in. and an ultimate elongation of 825 per cent. These values compare favorably with the average values reported by the Crude Rubber Committee for rubber compounded with 0.5 part of stearic acid in place of 0.55 part of zinc stearate and 6.0 parts in place of 5.95 parts of zinc oxide, all of the chemicals being incorporated by the conventional milling method. The reported values average 3265 lbs. per sq. in. and 810 per cent ultimate elongation for vulcanizates cured under the same conditions.

*Pilot-Plant Experiments.*—On the basis of preliminary laboratory experiments, an investigation of the precuring step was made with pilot-plant equipment, where better control of reaction conditions was possible. These experiments were made in steam-heated, internal-type mixers having capacities of 0.5, 1.5, 8, and 20 pounds, and provisions were made for removal of benzene.

It was found that, to obtain an easily controlled reaction, relatively high accelerator and low sulfur ratios were desirable, such as shown in Formula No. 6. When this formulation was used, a precured stock could be made which contained 0.4–0.6 per cent combined sulfur. Higher percentages of combined sulfur, such as were obtained in stocks using more than 0.6 per cent free sulfur in the initial solution compounding step, resulted in stocks that were too nervy and tough for proper milling. The procedure used throughout the pilot plant investigation was essentially the same as that described below when a Loomis Internal Mixer of approximately 20 pounds' capacity was used.

FORMULA No. 6

	Added in Solution (precure)	Added on rolls	Final composition
Rubber	100.	....	100.
Sulfur	0.6	2.9	3.5
Mercaptobenzothiazole	0.75	0.25	1.0
Diphenylguanidine	0.3	0.5	0.8
Zinc stearate	5.5	....	5.5
Flectol-H	0.5	....	0.5
Resins	3–7	....	3–7
Zinc oxide	....	5.5	5.5
Carbon black (Statex)	....	50.	50.

Chemicals were added to the benzene-rubber syrup, and the mixture was heated and allowed to flow into the mixer equipped for vacuum removal of benzene and with steam-heated blades and sides. After removal of benzene the temperature of the mix was allowed to rise to approximately 250° F, where the material began to set up appreciably. The temperature rose to about 280° F after about 15 minutes' additional heating. Exact temperature and time control at this point was not necessary. The precured material was then cooled rapidly and uniformly and discharged from the mixer.

Formula No. 6 was found to give consistently good results, and several hundred pounds of goldenrod rubber were processed in this manner. Formula No. 6 shows graphically a flat-curing stock prepared in a typical pilot plant run. The improved quality of this stock over the laboratory prepared stocks is evident.

It should be pointed out that with Formula No. 2, that is, when stearic acid is used in place of zinc stearate, it is conceivable that the slowly reacting

TABLE III  
PHYSICAL TESTS OF GOLDENROD RUBBER

Test	Method	Range of values	
	<i>Tread Stocks*</i>		
Tensile strength	Scott	2500-3200 lbs. per sq. in.	
Ultimate elongation	Scott	450-600%	
Modulus at 500%	Scott	2500-3000 lbs. per sq. in.	
Hardness	Shore	60-65	
Abrasion	Du Pont	175-240 cc. per H.P.-hr.	
Tear	Crescent	440-500 lbs. per in.	
Permanent set		20-25%	
Density		1.14-1.15	
Rebound	Firestone	Room temp.	32%
		212° F	46-55%
	<i>Gum Stocks*</i>		
Hysteresis	Absolute	Room temp.	1.0
		280° F	0.3
Hysteresis	Torsional, Mooney and Gerke	Room temp.	0.07
		280° F	0.06

\* Gum stocks contain no carbon black in the formulation. In all other respects tread and gum stocks are identical.

composition could also be satisfactorily adapted to this procedure, permitting an easily controlled reaction at the higher temperatures. This point was not investigated, since the aforementioned pilot-plant work had already produced a raw rubber stock that contained a sufficiently small quantity of chemicals to permit considerable latitude in choice of final compounding chemicals for factory-scale handling by any commercial user of this product.

Bicycle tires were made by one of the major rubber companies, several hundred pounds of raw precured stock being used in a commercial test run. These fabricated tires have not been completely evaluated; however, it is significant that on the plant's testing wheels the tires made from goldenrod rubber lasted approximately three times as long as tires made from reclaimed rubber for the present market.

The ranges for results of other tests are shown in Table III. These results, although not comprehensive, indicate that a rubber stock of good quality can be processed from goldenrod rubber by using the solution compounding method.

## SUMMARY

A solution method of compounding rubber has been devised. It is particularly suitable for compounding a soft natural rubber such as that recovered from goldenrod, but it does not appear to be restricted to goldenrod rubber. No particular inherent disadvantage of solution compounding is indicated with hevea rubber. By proper choice of solvent and compounding chemicals, the interesting possibility is presented of improving the quality of those rubbers in which proper dispersion of chemicals is difficult. This method also shows possibilities of being a valuable research tool in the pretreatment of soft synthetic elastomers as a preliminary step to evaluation of their rubber-like qualities.

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## PHYSICAL-CHEMICAL INVESTIGATIONS OF GOLDENROD RUBBER. IV

### INCREASE IN VISCOSITY AND FORMATION OF PHOTOGELS BY IRRADIATION OF GOLDENROD RUBBER IN THE ABSENCE OF OXYGEN\*

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When a benzene solution of raw Hevea rubber in an ordinary glass container is irradiated by sunlight in the absence of oxygen, its viscosity increases until finally a gel forms<sup>1</sup>. This increase in viscosity is preceded by a slight decrease, which is attributed to oxidation by minute traces of oxygen. According to the accepted theory, the viscosity decreases until all available oxygen has been used up in oxidation or depolymerization, and then polymerization causes it to increase until finally a gel forms. If depolymerization has progressed too far, that is, if the viscosity is too low, gelation does not take place.

The viscosity of goldenrod rubber is much lower than that of Hevea rubber; for a 0.175 per cent solution in benzene at 25° C, the absolute viscosity values are approximately 0.7 and 1.8 centipoises, respectively<sup>2</sup>. It has been found, however, that photogels can be formed from goldenrod rubber, with, and sometimes without, added activators.

A benzene extract of acetone-extracted goldenrod (*Solidago leavenworthii*) leaves, obtained in connection with the Emergency Rubber Project from the pilot plant in this Laboratory, and containing no antioxidant, was diluted to a concentration of about 3 per cent, and clarified by slurring with 3 grams of Merck's activated charcoal per 100 cc. and filtering, the whole procedure being carried out in an atmosphere of carbon dioxide. The exact concentration of the final solution, ascertained by a total-solids determination, was 2.91 grams per 100 cc.

In the following experiments 10-cc. aliquots of this solution were mixed with various activators and sealed off under vacuum in Pyrex-glass tubes. The weight of the activator was 5 per cent of the weight of the rubber, except in the experiments with chlorophyll and with carbon tetrachloride. In the latter case, 5 cc. of carbon tetrachloride was added to 5 cc. of the benzene solution. When chlorophyll was used, 1 mg. of chlorophyll was added for each 250 mg. of rubber (0.4 per cent). In all cases the samples were introduced into the Pyrex exposure tubes by a capillary-tipped funnel. The solutions were frozen solid in a slush of solid carbon dioxide and alcohol, evacuated to a pressure of about 0.2 mm., remelted, reëvacuated to eliminate most of the oxygen, and then sealed off.

A test run was made for a number of activators to determine the gelling time in sunlight. The results were as follows: benzophenone, less than 4.5 hours; benzaldehyde, less than 4.5 hours; carbon tetrachloride, 7 hours; benzoyl

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peroxide, 8 hours; maleic anhydride, 14 hours; chlorophyll, 65 hours; and quinone, 108 hours. A blank containing no activator did not gel after 108 hours. In a previous experiment, however, in which a different goldenrod rubber solution was used, a blank gelled in 10 hours. A similar inconsistency in the behavior of various goldenrod rubber solutions has been noted in the irradiation experiments in the presence of oxygen. This inconsistency de-

TABLE I  
IRRADIATION OF GOLDENROD RUBBER IN ABSENCE OF OXYGEN

Activator	Time exposed hours	Absolute viscosity of 0.175 per cent solution in benzene at 25° C centipoises	Precipitation value at 25° C cc.
Benzophenone	0	0.700	4.45
	$\frac{1}{2}$	0.681	4.75
	1	0.170	4.55
	2	0.731 (incipient gelation)	4.55
	4	(gel)	
Carbon tetrachloride	0	0.684	4.45
	$\frac{1}{2}$	0.679	4.45
	1	0.680	4.40
	2	0.674	4.30
	3	0.725	4.30
	4	0.728	4.30
	5	0.736	4.35
	6	0.765	4.30
	7	(gel)	
Benzoyl peroxide	0	0.665	5.05
	1	0.683	4.90
	2	0.685	4.85
	3	0.690	4.80
	4	0.685	4.75
	5	0.697	4.70
	6	0.691	4.70
	7	0.696	4.65
	8	0.716	4.70
	9	(gel)	
Maleic anhydride	0	0.694	4.40
	$\frac{1}{2}$	0.679	4.50
	1	0.689	4.65
	3	0.695	4.60
	5	0.710	4.65
	7	(gel)	
	10	0.771	4.70
	15	(gel)	

ended on the active components that remained in the solution after the treatment with activated charcoal<sup>3</sup>.

A series of tubes for each of a number of these activators was exposed to sunlight for different periods of time, one tube of each set being kept in the dark as a blank. After exposure the tubes were stored in the dark until they were opened and tested. Six cc. of each of these solutions was diluted to 100 cc. to make a 0.175 per cent solution of rubber. In the sample with carbon tetrachloride, 12 cc. was diluted to 100 cc., to give the correct final concentration. Aliquots were then used for the measurement of the absolute viscosity at 25° C

by means of a modified Ostwald viscometer, and also for determination of the precipitation value. The precipitation value<sup>2</sup> is a measure of the precipitability, being defined as the number of cc. of absolute ethyl alcohol required at a given temperature to produce a cloud point in 10 cc. of a clarified benzene solution containing 0.0175 gram of rubber sample.

The results are given in Table I. The initial values for the viscosity and precipitation value of the different solutions differed slightly, either because of the mere presence of the activator in the solution or because of some change caused by the activator during storage in the dark.

In each case, continued irradiation caused an increase in the viscosity and resulted finally in gelation. With the exception of the benzoyl peroxide sample, this increase was preceded by an initial decrease in viscosity. In the latter case this initial decrease might actually have occurred during the first hour, at the end of which the first sample was taken. Since the gel which finally formed was practically insoluble in benzene, its viscosity and precipitation value could not be determined.

Formation of rubber hydrocarbon polymers of higher molecular weight by irradiation would be expected to result in a higher degree of precipitability; that is, the precipitation value would be expected to decrease as the viscosity increased. This seems to be the trend for the carbon tetrachloride and the benzoyl peroxide samples. In the case of maleic anhydride, however, the precipitation value actually increased, though the absolute viscosity increased from 0.694 to 0.771 centipose. This corroborates the opinions of Stevens<sup>4</sup>, Naunton<sup>5</sup>, and Farmer<sup>6</sup> that the formation of photogels is not the result of a simple polymerization, and that it may sometimes involve condensation with the activator.

### SUMMARY

The viscosity of goldenrod rubber can be increased until gelation takes place by irradiation of its benzene solution in the presence of catalysts and in the absence of oxygen. Benzophenone, benzaldehyde and carbon tetrachloride seem to be the best of the activators tested.

### ACKNOWLEDGMENT

The authors are indebted to Florence B. Kreeger for determining some of the precipitation values given in the table.

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## "RUBBER ACID" DAMAGE IN FIRE HOSES \*

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In a brief reference, Crosby, Fiske and Forster<sup>1</sup> mentioned that a common cause of hose failure in rubber-lined fire hoses may be due to sulfuric acid formed from sulfur present in hoses when these are not properly dried. Such damage, apparently, was almost unknown in Great Britain before the War, but has recently been much in evidence. According to Phillips<sup>2</sup>, "rubber acid" is produced, and its damage observed chiefly in fire stations which lack adequate draining and drying facilities. It would appear to affect primarily, if not exclusively, rubber-lined fire hose.

When rubber-lined hose is stored after use, without preliminary drainage and drying, there is invariably left in it a certain amount of water, and when such hose is examined during storage, it is found to contain a liquid; commonly the amount is no more than a quarter of a pint. This liquid is not infrequently discolored brown. It is often slightly turbid and markedly acid; the degree of acidity tends to increase with duration of storage. On examination the acid proves to be sulfuric acid.

When rubber acid is accidentally spilt over the canvas surface of the hose, or over any other cellulosic fabric, rapid tendering occurs, a process which becomes accelerated with drying of the fabric. When spilt over a concrete floor, the rubber acid may cause corrosion of the floor surface and evolution of carbon dioxide gas bubbles.

Phillips<sup>2</sup> has given some data illustrating the importance of the damage caused by rubber acid to the hose, and, as an immediate remedy, advocated thorough draining of the hose after use. In a subsequent communication<sup>3</sup>, Phillips and his collaborators described an examination of three-hundred hose bursts, representing damage throughout Great Britain. More than 50 per cent of these bursts were due to rubber acid damage. They record also that rubber-lined hose of British, Canadian and American origin are equally subject to the fault, and that the concentration of sulfuric acid found in the hose liquor may reach a figure of about 1 per cent.

Phillips and his collaborators state that the opinion has been advanced that production of acid is due to the inclusion in the hose rubber of an excessive amount of free sulfur, which, in the presence of water and air, becomes oxidized to yield sulfuric acid. However, the well-known resistance of elemental sulfur to autooxidation at atmospheric temperatures seemed, on the face of it, to preclude this explanation. On the other hand, microorganisms had been observed in numerous samples of hose liquid, and since there is well-established evidence to show that in the presence of certain microorganisms, elemental sulfur can be oxidized to sulfuric acid at atmospheric temperatures, it was logical to keep this possibility in view and to ask the Chemical Research Laboratory to examine it.

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The initial samples of hose liquor were drawn under aseptic conditions from rubber-lined hoses from three fire stations in the Kingston (Surrey) district.

Details of these samples are given in Table 1.

TABLE 1

Station	Sample No.	Appearance of liquid	Reaction of liquid to litmus	pH of liquid	Hose last used
A	1	Colorless	Neutral	7.1	2 days
	2	Faintly discolored and turbid	Neutral to only slightly acid	7.0	previously
	3	Strongly yellow and turbid	Acid	1.0	2 days previously
B	4	Colorless	Neutral to only slightly acid (about $\frac{1}{2}$ gallon)	7.0	At least 6 months
	5	Colorless and somewhat turbid	Neutral to only slightly acid (about 1 quart)	7.1	At least 7 days
C	6	Brown	Acid	1.0	At least 4 months

The presence of microorganisms in the various samples was confirmed both by direct microscopic examination and by cultivation on ordinary nutrient agar, wort agar and thiosulfate agar, the latter being a medium free from organic substances and recommended by Waksman<sup>4</sup> for the cultivation of sulfur-oxidizing bacteria.

The microflora taken from the six samples of rubber acid and found capable of growth on ordinary nutrient agar comprised several forms, all of them with their natural habitat in soil and water. Their numbers ranged between two and fifteen million cells per cc. of hose liquor, except in Sample 6, where they were completely absent. The highest number occurred in Sample 2. None of them was of a type capable of oxidizing elemental sulfur.

On wort agar only four types of fungi developed: a black fungus so far unidentified; another with white mycelium, possibly a *Cephalosporium* species; a black *Dematium* species and a pink *Torulopsis* species. Their numbers did not exceed 70,000 cells per cc. in any of the rubber acid samples, and were no more than 20 per cc. in Sample 6.

The *Cephalosporium* species was found in Samples 1 and 2; the unidentified fungus in Samples 3, 4, 5 and 6; the *Dematium* species in Samples 1 and 4 and the pink *Torulopsis* species in Sample 4. Only the black fungus, therefore, could have been associated with acid production. However, since it did not appear on any of the thiosulfate agar media, it is unlikely, to say the least, to have played a major part in sulfur oxidation.

The organisms which grew on the thiosulfate agar were restricted to no more than five types, all of them short, nonspore-forming rods. Their numbers in the various acid samples were very much of the same order, ranging from 13 to 19 million cells per cc. of hose liquor, except in Sample 6, where only 5 million cells were counted.

Each of these types was tested for its sulfur-oxidizing power by inoculating it into a medium containing inorganic salts and free sulfur. On this medium only two of them, isolated from hose liquor Samples 3 and 6, grew rapidly, and in less than a week rendered the liquid turbid and acid, with a drop in the original reaction of the medium from pH 4.6 to pH 1. The acid produced was

identified as sulfuric acid. Of the remaining types of short rods growing on thiosulfate agar, it should be mentioned that they grew well also on ordinary nutrient agar. Those from liquors nos. 3 and 6, which produced acid from elemental sulfur, did not do so.

The remaining four samples of hose liquid, from which sulfur-oxidizing bacteria had not been isolated by the direct method employed, were inoculated into an inorganic liquid medium containing free sulfur. It was suspected that the failure to isolate sulfur-oxidizing bacteria from these samples might have been due to their containing too few cells. By introducing the original hose liquors into a medium specially adapted for the growth of sulfur-oxidizing bacteria, it was hoped to increase their numbers and thus to facilitate their isolation. However, after incubation of the inoculated special media for 14 days at 30° C only one of these, that inoculated with hose liquor no. 4, gave rise to acid. From this sample it was possible to isolate typical sulfur-oxidizing bacteria. The others remained unchanged in reaction and showed no growth of microorganisms. It is probable, therefore, that these samples (Nos 1, 2 and 5) had not contained the organisms looked for.

It had been possible, therefore, to isolate sulfur-oxidizing bacteria from only 50 per cent of the hose liquors examined, implying either that these organisms may not be necessary for acid formation, or that these samples of liquors in which the organisms had not been found, and presumably had not been present, would have failed to become acid in any event. On the available information it is not possible to decide which of the two alternatives is correct, though one deduction that can be made from the collected data seems to point in favor of the latter explanation.

The inconclusiveness of the results thus far obtained, which incidentally were unlikely to be improved upon by an analysis of further samples of hose liquor, made it desirable to test the hypothesis of a microbiological origin of rubber acid from a different angle, and to establish whether water introduced into rubber-lined hose would invariably become acid, if it contained sulfur-oxidizing bacteria.

An experiment was set up for this purpose, in which tap water containing sulfur-oxidizing bacteria was introduced into sections of hose about 2 feet long. Sections from three hoses were chosen, two from new hoses, the other from a hose already in service which had developed rubber acid. Each section was bent in the shape of a U and into each, 25 cc. of test water, containing test bacteria, were introduced. The sections were then closed with clamps to reduce evaporation, and incubated at room temperature. Each section was opened daily to admit oxygen and also shaken to keep the inner rubber surface wet. As control, a sterile section was taken from each hose. Into each of these, 25 cc. of sterile tap water was introduced, but no bacteria.

Table 2 shows the rate of change in pH values of the water contained in the various sections during 14 days of incubation.

There is an interesting deviation in the expected results tabulated in Table 2. One of the new hoses apparently did not respond as expected to the presence of sulfur-oxidizing bacteria. This was a hose in which the free sulfur present amounted to less than 0.1 per cent. Apart from this it was possible to confirm that the presence of sulfur-oxidizing bacteria is essential for the production of acid hose liquor.

In a further experiment with sections of the No. 2 new hose, in which, in addition to sulfur-oxidizing bacteria, free sulfur was added to the water intro-

TABLE 2  
CHANGES IN pH VALUES OF WATER KEPT IN RUBBER-LINED FIREHOSES

No.	Description	pH of water after incubation for			Percent- age free sulfur in hose
		0 days	1 day	14 days	
1	New hose (sterile)	7.4	7.4	7.4	0.2
1a	New hose + sulfur-oxidizing bacteria	6.0	6.2	1.6	0.2
2	New hose (sterile)	7.4	7.4	7.4	<0.1
2a	New hose + sulfur-oxidizing bacteria	6.0	6.2	6.2	<0.1
3	Old hose (sterile)	7.4	7.4	7.4	0.1
3a	Old hose + sulfur-oxidizing bacteria	6.0	6.4	2.7	0.1

duced into a sterile section, it was possible to show that the failure of acid production was due not to any inhibitory properties possessed by this hose, but to the presence of insufficient free sulfur. For in this additional experiment the pH value of the water contained in the section dropped to below 1.2 in the course of 14 days.

It is clear, therefore, that there are two factors governing acid production in hose: first the presence or absence of the relevant bacteria; and, secondly, the presence of a sufficiency of free sulfur. This latter apparently should not fall below 0.1 per cent, calculated on the rubber lining. If the figures of Table 2 may be taken as substantially correct, production of acid will be proportional to the percentage of sulfur present, other factors being favorable.

The presence or absence of sulfur-oxidizing bacteria will probably be governed largely by the type of water passing through hose when in use; and it was thought relevant, therefore, to examine fire-fighting water supplies for the presence of these organisms.

On inquiry it was found that much of the water available to the National Fire Service in the London district is taken from static supplies, these being replenished from the River Thames, or from local canals and ponds. Water taken direct from the mains is not used when other supplies are available.

An analysis of twenty-five samples of water from different sources of supply, including mains water, revealed that thirteen contained sulfur-oxidizing bacteria. Only two of the samples of mains water out of six examined contained these organisms. The percentage, therefore, of the crude waters used which contained these bacteria was no less than 58 per cent. The observation may perhaps give a clue to the frequency with which rubber acid is likely to be found in hose.

The presence of sulfur in rubber-lined hoses was found on inquiry to vary very considerably. Prewar hose specifications, according to Phillips<sup>2</sup>, limited the free sulfur content in hose lining to 1 per cent in Great Britain and to 1.25 per cent in the United States. But these data are not a reliable guide, for recent analyses of twelve American samples showed the content to vary between 0.06 and 0.7 per cent. Similar variations are likely to occur in hose made in Britain and in Canada. From the data given in Table 2 it would appear that a free sulfur content of 0.1 per cent is sufficient to produce some acid, and that 0.2 per cent causes marked acid production. A permitted minimum of 1 per cent of free sulfur is, therefore, a gross excess, and can be expected to lead to acid production whenever the appropriate bacteria are present.

## CONCLUSIONS

The conclusions to be drawn from the experiments which have been carried out would appear to be that:

The production of rubber acid in hose is due to the activity of sulfur-oxidizing bacteria of the *Thiobacterium thiooxidans* group.

Such acid will invariable be formed in rubber-lined hose which is stored with the linings wet, when the responsible bacteria are present, and when the free sulfur content of the hoses exceeds 0.1 per cent.

If acid production is to be prevented, it is necessary to ensure, either that the rubber-lined hose is stored dry, or that its content of free sulfur is less than 0.1 per cent.

The alternative of preventing the introduction of the causal bacteria does not appear practicable, since the water used in fire-fighting is a frequent habitat of these bacteria.

In a series of additional experiments it was established that various organic sulfur compounds, commonly used in the vulcanization of rubber, failed to give rise to acid production, even in the presence of sulfur-oxidizing bacteria.

## ACKNOWLEDGEMENT

Thanks are due to the officers and men of the National Fire Service, and especially to Company Officer W. E. Gage, Hose Officer, No. 38 Fire Force, who assisted us in obtaining the necessary experimental material and certain data required for this investigation. The work was carried out on behalf of the Director of Scientific Research, Ministry of Home Security, and is published with the approval of the Department of Scientific and Industrial Research and the Ministry of Home Security.

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# INVERSE CORRELATION BETWEEN RUBBER HYDRO-CARBON AND A CRYSTALLINE FRACTION ISOLATED FROM LATEX OF *CRYPTOSTEGIA GRANDIFLORA* \*

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## INTRODUCTION

A crystalline fraction has been isolated from dried latex of *Cryptostegia grandiflora*. Available data indicate that there is an inverse correlation between this crystalline fraction and the rubber hydrocarbon in the latex. This relation may afford an opening wedge into the problem of rubber formation in plants.

*C. grandiflora*, a member of the Asclepiadaceae, is one of several plants being studied as an emergency source of rubber. The plant is either a large shrub or a vine, depending on available support for vining. In addition to foliage branches, it produces relatively long, rapidly growing, mostly unbranched leaders, which tend to twine around any available support. These leaders, or whips, as they sometimes are called, usually originate from lateral buds along the thicker main stems which form the body of the shrub. Their diameter near the tip is 2-3 mm., widening to 15-20 mm. near the base. For nearly one-third of their length from the tip they are either completely leafless, or the small unexpanded leaves are adnate to the whip. In this region the whips usually are succulent, very slightly lignified, and have a large proportion of pith and cortex, whereas the lower part of the whip is woody, lignified, and with proportionally little pith. A more complete description of the plant is given by Polhamus, Hill and Elder<sup>1</sup>. Failing to twine on a support, the whip may grow to a length of 12-15 feet before bending downward from its own weight. As the whip continues to grow and bend, short, leafy, lateral branches are produced, and it becomes increasingly woody. The weight of these branches in turn contributes to the further bending of the whip down within the body of the shrub. New whips, which often originate from old foliated ones, are continually produced, and replace the older ones. Cutting off the tips of the whips before they bend downward and collecting the exuding latex has been one suggested method of utilizing the plant as an emergency source of rubber. This general procedure, called "whip bleeding", was the manner in which most of the latex samples used in this investigation were collected.

## METHOD

During the course of yield determinations by whip bleeding from March 1943, through July 1944, 157 latex samples were collected. These were dried

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to constant weight in a thermostatically controlled oven at 60° C, instead of being coagulated as usual by some such agent as alcohol or water. For the studies reported here, the importance of drying the latex instead of using a coagulating agent cannot be overemphasized. In common practice, after the use of a latex-coagulating agent, the serum is usually discarded, and only the coagulate is analyzed. While this may be satisfactory for quality determinations of the coagulate, it yields physiological information of limited value, since a portion of the latex is discarded with no further consideration.

The samples represented collections of extremely wide diversity. They were secured from the vicinity of Brownsville, Texas, and Ciudad Victoria, Tamaulipas, Mexico. Some of the collections were composite yields of latex from single whips on individual plants, bled four to seventeen times consecutively; others were pooled yields from various amounts of successive bleedings of 20 to 50 plants. Some of the samples were from plants 7 months old; others were from plants estimated to be 15 years old. In most collections the whips were of the type just described, although a few samples were from foliage branches of small diameter (0.25 inch or less), very old bent-down whips, thick (1.5 inch diameter) basal foliage stems, and seed pods. All collections were from the above-ground portion of the plants. Because of the extremely wide diversity of the collections, the whip internode in which the bleeding was made, the number of previous bleedings of the whip, the time interval between bleedings, the time of day of the bleeding, the season of the year, and the amount of whip cut away per bleeding were factors varying from sample to sample.

The oven-dried latex samples were analyzed for rubber hydrocarbons by a bromination technique and for insolubles by a direct gravimetric determination. These methods were kindly supplied by private communication from C. O. Willits of the Eastern Regional Research Laboratory, and are as follows.

Accurately weighed samples of the dried latex, sometimes called "total latex solids", are cut into small pieces, placed in tared centrifuge tubes, and treated with benzene containing 1 per cent of trichloroacetic acid. After standing for three days, with occasional stirring, insoluble substances are separated by centrifuging and washing with benzene. The benzene solution and washings are made to volume with benzene, and aliquots are brominated, using a solution of bromine and iodine in carbon tetrachloride. The "rubber tetrabromide" so formed is precipitated with 95 per cent ethyl alcohol, filtered, dried, and weighed. The percentage of rubber in the sample is calculated by multiplying the weight of rubber tetrabromide by the empirical factor of 0.285.

The substances insoluble in benzene which remain in the centrifuge tubes are thoroughly extracted several times with acetone. The insolubles still remaining are separated by centrifuging, dried at 60° C, and weighed. Insolubles prepared by this method—using trichloroacetic acid in the benzene extraction<sup>2</sup>—have been shown to be completely free of rubber hydrocarbons.

By these methods, "insolubles" in latex total solids are defined as substances which are insoluble in either acetone or benzene, and "rubber hydrocarbons" are defined as benzene-soluble substances which form bromides insoluble in 95 per cent ethyl alcohol. The insolubles and rubber hydrocarbons are each directly determined, percentages being based on original weight of latex sample dried at 60° C.

## RESULTS AND DISCUSSION

Analyses of the diverse assortment of latex samples indicated that they varied in such a way that the percentage of rubber hydrocarbons was, without

exception, inversely correlated with the percentage of insolubles (Figure 1). The correlation coefficient, significant at the 1 per cent level, was  $-0.9371$ . Apparently this inverse correlation was a linear relationship. From these analyses, using the method of least squares<sup>3</sup> for the computation of regression averages, it was possible to calculate the equation:  $R\% = 77.8 - 0.809 I\%$ , where  $R$  = rubber hydrocarbons and  $I$  = insolubles. The regression coefficient, significant at the 1% level, is  $-0.809$ . This equation defines the regression line  $RI$  (Figure 1), which has intercepts on the rubber hydrocarbons and insolubles axes of 77.8 and 96.2, respectively, and is calculated from 149 analyses. These are theoretical limits based on extrapolation, and are subject to experimental error. The standard error of the estimate was 2.6 per cent, which represents graphically an average of the vertical distances of the dots from  $RI$ . Table 1 gives the analyses of twenty-five of the 149 samples represented in Figure 1.

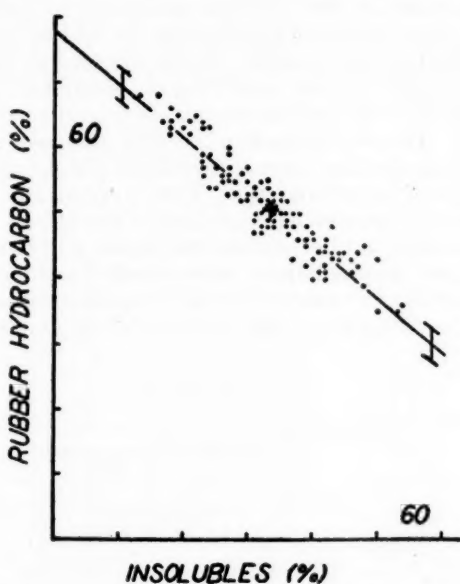
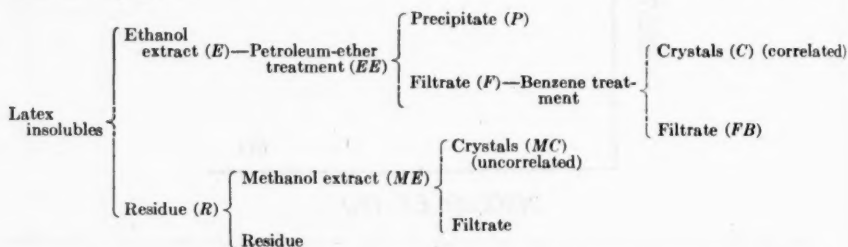


FIG. 1.—Inverse correlation between percentage of rubber hydrocarbons and percentage of insolubles in dried latex of *C. grandiflora*. Regression line, with standard error, calculated from 149 latex analyses. Cross indicates average point.

Analyses of twenty-three additional samples of latex, dried at 60° C, were made by a direct extraction method described by Hall and Goodspeed<sup>4</sup>. The determined percentages of rubber hydrocarbons and insolubles for each sample were located on the calculated  $RI$  regression line. These analyses, however, were not used in computation of the regression line, nor are they shown in Figure 1, since by this method of analysis the insolubles are determined indirectly. Latex samples of average resin content, analyzed by this method, might appear to have—within the limits of standard error of the regression line  $RI$ —rubber hydrocarbons and insolubles inversely correlated, solely because of incomplete extraction of rubber hydrocarbons. For this reason an inverse correlation based on analyses by this method may or may not be correct, depending on the completeness of the extractions.

To concentrate the substances present in the insolubles which caused the inverse correlation with rubber hydrocarbons, a survey was made to discover solvents which could extract them from the "insolubles". It was found that they were dissolved by water, by 95 per cent ethyl alcohol, and by absolute ethanol. Further trials indicated that if the insolubles were dried to a constant weight at 100° C before extraction with ethanol, an additional separation of this extract (*E*) into two portions was possible by a fractional precipitation technique. The separation of latex insolubles into a crystalline fraction inversely correlated with rubber hydrocarbons and noncorrelated fractions is shown in the following schematic representation. Letters in parentheses identify the fraction with the corresponding discussion in the text. The first fraction was obtained by adding petroleum ether to the ethanol until an oily, brown, flocculent precipitate formed (*P*). Failing to form a precipitate on addition of a volume of petroleum ether equal to that of the ethanol, the solution (*EE*) was partially evaporated at 100° C until a precipitate formed. In some cases it was necessary—even after this evaporation—to add more petroleum ether to change the solubility relationships in the solution so that a precipitate would form. After quantitatively separating the precipitate from the solution, this same treatment was repeated on the filtrate several times until no further precipitate formed. The second fraction was then obtained by adding benzene to the filtrate (*F*) until the formation of crystalline platelets began (*C*). Here, as with the addition of petroleum ether, if no crystallization began after the addition of a volume of benzene equal to that of the filtrate, it was necessary to evaporate the solution until crystallization began, and in some cases to add more benzene. These manipulations were repeated until no further crystal formation was obtained. Evaporation of the remaining filtrate (*FB*) yielded a residue which was less than 1 per cent of the original sample. This was considered negligible.



The ethanol extract (*E*) of insolubles from latex samples low in rubber hydrocarbons often was dark reddish brown, while from those high in rubber hydrocarbons it was straw-yellow color. After complete precipitation of the brown precipitate (*P*) by the addition of petroleum ether, the filtrate (*F*) was usually light yellow. This color change was indicative of the completion of precipitation. If the precipitation was not complete, crystals (*C*) contaminated with a slight amount of brown color resulted. This was removed by redissolving the crystals in a small volume of hot ethanol, adding powdered activated charcoal to adsorb the brown color, filtering, and then repeating the crystallization procedure. A loss of about 40 per cent usually occurred from this treatment, thus making it unsatisfactory for a quantitative determination of the crystals.

Identification of the crystals (*C*) from the ethanol extract is not yet complete, but a few properties have been determined. They are white, slightly

bitter-tasting, and strongly birefringent. They begin to char at 180° C, and melt between 234° and 236° C. Crystals isolated from the serum of auto-coagulated latex of *C. grandiflora* have been reported to have a bitter taste and to melt at 236–7° C<sup>5</sup>, and so they may be the same as those described here.

To determine the extent to which either the flocculent precipitate (*P*) or the crystalline fraction (*C*) might be inversely correlated with rubber hydrocarbons, eight latex samples of known composition were selected. Aliquots of these were reanalyzed to check the previous determinations. These samples varied in percentage of rubber hydrocarbons from 38 to 62, and in percentage of insolubles from 47 to 19. Their selection thus represented a relatively wide distribution along the rubber hydrocarbons insolubles regression line. The insolubles obtained by the analytical method from these samples were extracted by using four portions of absolute ethanol with stirring. After extrac-

TABLE 1

NUMERICAL DATA FOR TWENTY-FIVE OF THE 149 CRYPTOSTEGIA GRANDIFLORA LATEX TOTAL SOLIDS ANALYSES SHOWN GRAPHICALLY IN FIGURE 1. LATEX OBTAINED BY WHIP BLEEDING UNLESS OTHERWISE INDICATED

Sample no.	Latex source		Collection date	Latex analyses (%)		
	Bleeding	Other data		Rubber hydrocarbons	Insolubles	Undetermined (remainder)
106	2nd	Whips defoliated by hand	2/25/44	35	53	12
59	8th	Fifteenth internode	8/28/43	36	54	10
121	2nd	Entire plant defoliated	2/25/44	37	45	18
37	16th	At 24-hr. intervals	8/29/43	39	48	13
99	7th	Entire plant defoliated	2/5/44	40	40	20
116	1st	Whips 2–3 ft. long	3/9/44	41	42	17
135	1st	Plants in 5-gal. container <sup>a</sup>	6/2/44	42	42	16
159	4th	At 24-hr. intervals, 6:00 P.M.	3/23/44	43	37	20
169	5th	Plants in 5-gal. containers	6/7/44	44	41	15
113	18th	At 48-hr. intervals	3/24/44	45	39	16
146	1st	2:00 P.M.	3/20/44	46	38	16
11	10th	At 72-hr. intervals	9/10/43	47	36	17
26	6th	At 24-hr. intervals	8/19/43	48	34	18
148	2nd	At 24-hr. intervals, 6:30 A.M.	3/21/44	49	33	18
23	4th	At 24-hr. intervals	8/17/43	50	35	15
151	2nd	At 24-hr. intervals, 6:00 P.M.	3/21/44	51	34	15
131	1st	Sixth internode	5/11/44	52	32	16
2	2nd	Eighth internode	8/15/43	53	34	13
145	1st	Third internode, whips 10 ft. long	6/15/44	54	31	15
144	1st	Third internode, whips 6 ft. long	6/15/44	56	27	17
28	6th	At 24-hr. intervals	8/19/43	58	23	19
166		Seed pods, nearly mature	3/12/44	59	23	18
101	8th	At 48-hr. intervals	8/28/43	63	18	19
109	14th	At 48-hr. intervals, two bleedings per internode	9/9/43	65	19	16
110	14th	At 48-hr. intervals, one bleeding per internode	9/9/43	68	13	19

tion, the residue was washed with an additional small portion of absolute ethanol, and the extracts and washings were combined for each sample. These were then separated into crystalline (*C*) and noncrystalline (*P*) fractions by the technique described. The crystalline fraction was inversely correlated with rubber hydrocarbons, but the noncrystalline portion was not correlated (Figure 2). The coefficients of correlation for rubber hydrocarbons and crystals, and for rubber hydrocarbons and noncrystalline portion, were  $-0.9056$  and  $-0.5753$ , respectively. The correlation coefficient for crystals was significant at 1 per cent, but that for the noncrystalline portion lacked significance at 5 per cent. The equations, with standard error of the estimate, for the regression of percentage rubber hydrocarbons on percentage of insolubles, ethanol extract (*E*), and crystals (*C*), as given in Figure 2, are:  $R = 75.5 - 0.780 I$ ,  $\pm 2.6$ ;  $R = 70.0 - 1.025 E$ ,  $\pm 3.2$ ; and  $R = 68.8 - 1.218 C$ ,  $\pm 3.8$ , respec-

tively. The equation for the regression of percentage precipitate ( $P$ ) on percentage rubber hydrocarbons is:  $R = 86.4 - 11.4 P, \pm 1.1$ . This experiment was repeated on three additional latex samples with similar results.

While the crystalline fraction appears to account for the major portion of the observed inverse correlation between rubber hydrocarbons and insolubles, whether or not it alone accounts for the entire correlation is not known—since an inverse correlation was observed between rubber hydrocarbons and the insoluble residue ( $R$ ) left after ethanol extraction. The correlation coefficient was  $-0.7537$ , significant at 5 per cent. The regression of rubber hydrocarbons on this residue is  $73.6 - 1.779 IR$ , where  $IR$  equals the insolubles not extracted by ethanol. Standard error of the estimate is  $\pm 5.09$ . The regression coefficient is also significant at 5 per cent.

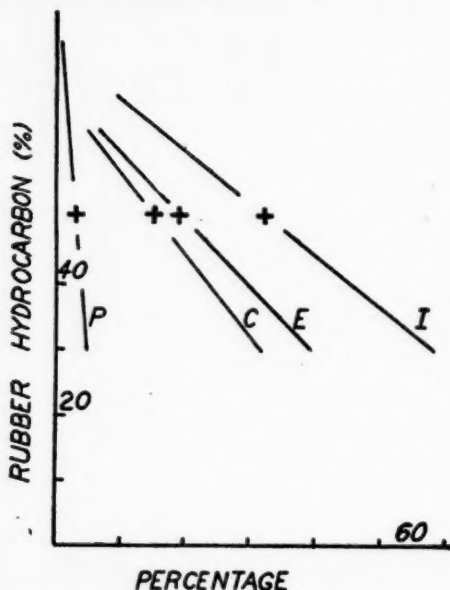


FIG. 2.—Inverse correlation in dried latex of *C. grandiflora* between percentage of rubber hydrocarbons and percentage of: insolubles, regression line  $I$ ; ethanol extract of insolubles, line  $E$ ; and crystalline fraction from ethanol extract, line  $C$ . Crosses indicate average points in each case. Correlation coefficients for these regressions are  $-0.9557$ ,  $-0.9337$ , and  $-0.9056$ , respectively (significant at 1%). Precipitate from ethanol extract (line  $P$ ) not significantly inversely correlated with rubber hydrocarbons.

Since the correlation between rubber hydrocarbons and insoluble residue ( $R$ ) could have resulted from incomplete ethanol extraction of the insolubles, more complete extractions were made by shaking the insolubles overnight in ethanol, following three 10-minute extractions with hot ethanol. These were carried out on the insolubles from three large lots of latex which were being used to prepare a quantity of crystals. The overnight shaking extraction was repeated two additional times on new aliquots of insolubles from the same three lots, which had percentages of rubber hydrocarbons and insolubles of 37, 33; 45, 24; and 56, 12; respectively. The crystalline fraction ( $C$ ) was obtained from the extract by the fractional precipitation technique described. As in the previous experiment, the crystalline fraction ( $C$ ) accounted for the correlation of the extract ( $E$ ), but in every trial the extract still apparently failed to

contain all the correlated portion of the insolubles. The insolubles residue (*R*) remaining after ethanol extraction still had a very slight but significant inverse correlation with rubber hydrocarbons. Owing to mechanical difficulties, because of the large size of the lots, recovery of the insolubles from the oven-dried latex was incomplete. This located the regression line of rubber hydrocarbons on latex insolubles (Figure 3) slightly toward the left of the original line given in Figure 1. The slope of this line is the same as that of the original, however, since the determinations of rubber hydrocarbons were not changed by the size of the lots.

Further investigation of this apparently correlated residue (*R*) indicated that it was possible to separate it further by extraction with absolute methanol. From duplicate methanol extractions of the residue (*R*) from the three lots of latex, it was found that this extract (*ME*) was not correlated with rubber hydrocarbons. After extraction, crystal formation was readily induced by reducing

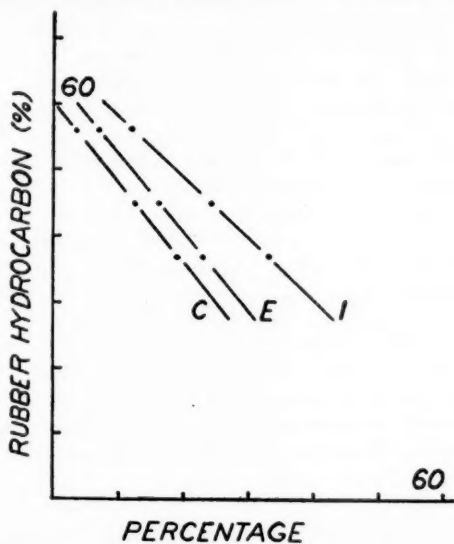


FIG. 3.—Inverse correlation in dried latex between percentage rubber hydrocarbons and percentage of insolubles (*I*); ethanol extract of insolubles (*E*); and crystalline fraction from ethanol extract (*C*).

the volume of the extract. These crystals (*MC*), like the methanol extract (*ME*), were not correlated with rubber hydrocarbons. Their properties and identity are being determined. It was clear, however, that these crystals differed from those obtained by the ethanol extraction, since these lacked birefringence. They were readily soluble in methanol and also very slightly soluble in ethanol. Because of their solubility in ethanol, the amount of ethanol extract (*E*) from insolubles will depend in part on the amount of these noncorrelated crystals (*MC*) present in the insolubles.

A further attempt was made to extract all the correlated substances from the insolubles with ethanol by using micro-Soxhlet extractors. Three insolubles samples of 200 mg. each were extracted 48 hours. The extraction was complete, as indicated by constant weight of the residue during the final 12 hours. During the extraction, crystals precipitated from the ethanol. These crystals lacked birefringence, were very readily soluble in methanol, and appeared to

be the same as those just described (*MC*). They amounted to 12.0, 2.9, and 5.4 mg. from the three latex samples which had 56, 45, and 37 per cent rubber hydrocarbons, respectively. In this way the ethanol extract (*E*) of insolubles from samples highest in rubber hydrocarbons was increased by this non-correlated portion over those from lower percentages of rubber hydrocarbons. Since some of these noncorrelated crystals (*MC*) probably also remained in the ethanol solution, when considered together with those which precipitated out, they could probably account for the convergence of the two regression lines—rubber hydrocarbons on insolubles and rubber hydrocarbons on extract—at the high percentage levels of rubber hydrocarbons (Figures 2, 3).

Methods are being investigated for more completely separating the two crystalline fractions (*C* and *MC*) found in the insolubles. While it seems possible that the crystalline fraction (*C*) from the ethanol extract may be the only one in the latex inversely correlated with rubber hydrocarbons, conclusive proof will await the development of its more selective isolation from the insolubles.

When fresh latex is dried on a sheet of glass, both the correlated ethanol fraction crystals (*C*) and the apparently noncorrelated "methanol" crystals (*MC*) are visible. The former may be seen readily with the naked eye, but the latter are usually apparent only on microscopic examination. That the "ethanol" crystals (*C*) are readily visible in latex dried in this fashion is not surprising, since they constitute 19 per cent of the total latex solids from latex which has 37 per cent rubber hydrocarbons.

The significance of the inverse correlation between rubber hydrocarbons and the crystalline fraction (*C*) extracted from the insolubles by ethanol is not known. The crystalline substance might be directly converted into rubber hydrocarbons within the plant and so be considered a "precursor" of rubber hydrocarbons; but it is equally possible that it might be a substance very indirectly related to rubber hydrocarbons. For example, it might be derived from the same source of materials as rubber hydrocarbons, and so in effect be indirectly related to them by competition for its origin. Identification of the crystals and physiological experiments in progress may indicate the role this substance has in rubber formation and latex physiology.

#### SUMMARY

1. Analysis of 157 samples of dried latex from above-ground portions of *Cryptostegia grandiflora* indicated a linear inverse correlation between the percentage of rubber hydrocarbons and the insolubles.

2. By extraction of the latex "insolubles" with absolute ethanol and fractional precipitation of the extract, an unidentified crystalline fraction was obtained which was inversely correlated with rubber hydrocarbons. It is possible that this crystalline fraction is the only one in the insolubles and latex inversely correlated with the rubber hydrocarbons.

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## COMPOSITION OF RUBBER FROM DIFFERENT BOTANICAL SOURCES \*

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Natural rubber from botanical sources other than *Hevea brasiliensis* now forms an appreciable proportion of the total rubber available to manufacturers in Allied countries.

The principal source of this wild rubber is the African continent, the home of Landolphia, Funtumia and other rubber-producing vines and trees.

### RUBBER HYDROCARBON CONTENT

The information given in Table 1 summarizes the general chemical characteristics of natural rubber from different botanical sources and, in particular, shows the amount of rubber hydrocarbon normally present in each type. Column 9 shows the values obtained by difference and column 10 those obtained by direct estimation, using the chromic acid oxidation method (*ASTM Bull. No. 120*, Jan. 1943, p. 23; *RUBBER CHEM. TECH.* 16, 660 (1943)). The difference method assumes that the nitrogen is present as protein with a factor of 6.25; and, in calculating the results, allowance is made for the nitrogen and ash in the material insoluble in boiling nitrobenzene (See Table II). The direct estimation calls for no special comment except that the samples required very thorough blending to obtain concordant results, and varied considerably in the time required for digestion with oxidizing mixture.

The calculated results for rubber hydrocarbon given in column 9 are within  $\pm 2$  per cent of those determined directly (Column 10).

All wild rubbers of commercial importance usually contain over 80 per cent rubber hydrocarbon, but none contains as much as Hevea. The substitution of African rubber for an equal weight of plantation Hevea, therefore, results in a loss of rubber hydrocarbon, but in most mixes used today, substitution is only partial and the loss is very small. The desirability of regarding 110 parts of wild rubber as the equivalent of 100 parts of plantation rubber is, however, worthy of consideration by compounders, particularly as the rubber hydrocarbon content of mixes is already cut as far as is consistent with reasonable quality.

### ACETONE EXTRACT AND ACID VALUE

Determinations of the fraction of the acetone extract which is readily soluble in ethyl ether and the acidity of the soluble and insoluble fractions, respectively, have proved useful in characterizing natural rubber from different botanical sources. The results obtained on the samples under discussion are given in Table III.

The method of preparation of the rubber often exerts a considerable influence on the percentage of the acetone extract and its acidity. For example, values ranging from a little over 1 per cent up to 4 per cent of acetone extract

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TABLE I  
RUBBER HYDROCARBON CONTENT

All values are expressed as per cent of moisture-free material; moisture ranged from 0.3% in Hevea smoked sheet to 1.3 in Ceara scrap.

Botanical origin	Country of origin	Mode of preparation	Acetone extract	Nitrogen $\times 6.25$	Ash	Nitrobenzene-insoluble		Rubber hydrocarbon	
						Total	Calculated already given in columns 5 and 6	Calculated by difference	Direct determinations
Hevea brasiliensis	Ceylon	Smoked sheet	3.1	2.2	0.2	0.1	0.1	94.5	94.8
Funtumia elastica	West Africa	Smoked sheet	8.7	7.8	0.7	10.0	3.9	78.9	80.2
Landolphia sp. (probably L. heudelotii)	French Guinea	Native; rubber washed and dried at M.O.S. depot	7.6	1.6	1.5	4.9	3.9	85.4	84.7
Landolphia sp. (probably L. thollonii)	French Equatorial Africa	"Root rubber," prepared in laboratory, stripped from the rhizomes in Africa, by treatment in a wooden rod mill and crepeing.	5.1	0.7	1.3	4.7	3.6	89.3	87.8
Manihot glaziovii (Ceara)	French Equatorial Africa	Tree scrap, washed and creped in laboratory.	3.2	5.8	1.9	5.1	2.3	86.8	84.9
Cryptostegia sp.	Madagascar	(a) Dried latex, washed and creped in laboratory. (b) Same sample after extraction with water.*	9.4	6.7	3.7	..	..	..	..
			8.5	1.6	0.5	..	..	75.5	73.9
Taraxacum kok-saghyz	Grown in Great Britain from Russian seed	Coagulation of rubber in the root by boiling in water, destruction of vegetable tissues by boiling caustic soda, washing and crepeing in laboratory.	5.7	2.3	3.1	8.7	5.3	83.6	85.3
Taraxacum krim-saghyz			5.0	2.6	3.6	..	..	..	84.2

\* This treatment removed 13.9% water-soluble material.

may be obtained for Hevea, according to whether the rubber has been well prepared or whether it has been carelessly treated under conditions allowing for the full play of oxidizing and bacterial agencies. Acid values likewise range from as low as 50 to over 300. Most wild rubbers have low acid values, and it may be necessary to add extra stearic acid to some mixes which contain an appreciable proportion of wild rubber.

Variation in acetone extract with Funtumia is from about 6.5 to 9 per cent, of which from 5.5 to 7 per cent is soluble in ether. The acid values of both ether-soluble and ether-insoluble fractions of the acetone extract are much

TABLE II  
ANALYSIS OF NONRUBBER MATERIAL INSOLUBLE IN NITROBENZENE

Type of rubber	Total %	Retained by screens of		Ash %	Nitrogen $\times 6.25$ %
		200-mesh %	40-mesh %		
Hevea brasiliensis	0.1	0.045	0.005	..	..
Funtumia elastica	10.0	0.045	0.01	5.6	56.25
Landolphia sp. (probably L. heudelotii)	4.9	0.51	0.06	20.9	..
Landolphia sp. (probably L. thollonii)	4.7	..	..	22.7	..
Manihot glaziovii (Ceara)	5.1	0.125	0.05	13.2	43.25
Taraxacum kok-saghyz	8.7	1.435	0.01	22.0	17.38

TABLE III  
ANALYSIS OF ACETONE EXTRACT

Type of rubber	Total %	Soluble in ethyl ether %	Acid value of	
			Ether- soluble fraction mg. KOH/%	Ether- insoluble fraction mg. KOH %
Hevea brasiliensis	3.1	2.6	208	40
Funtumia elastica	8.7	7.0	119	9
Landolphia sp. vine rubber (probably L. heudelotii)	7.6	4.4	96	53
Landolphia sp. "root rubber" (probably L. thollonii)	5.1	4.4	58	6
Manihot glaziovii (Ceara)	3.2	2.9	62	13
Cryptostegia sp.	8.5	6.4	28	8
Taraxacum kok-saghyz	5.7	5.5	84	..
Taraxacum krim-saghyz	5.0	4.8	93	3

lower than those for Hevea, and the ether-insoluble fraction often has hardly any acidity.

Similar values are found for Cryptostegia rubbers.

In the Landolphia vine rubbers, e.g., L. heudelotii and L. owariensis, from French West and Equatorial Africa, the acetone extract varies considerably, but is generally lower than in Funtumia, and is rather less soluble in ether.

Landolphia root rubbers have an extract of from 4 to 6 per cent, about three-quarters of which is soluble in ether.

Kok-saghyz rubber prepared from plants grown in this country gave acetone extracts of from 5 to 6 per cent, practically completely soluble in ether.

The acetone-soluble substances are somewhat fluid waxes, resins and acids, etc., which may have a mechanical softening effect on vulcanized products.

TABLE IV  
ANALYSES OF ASH

Type of rubber	Water-soluble components			Insoluble in water	
	Total ash % rubber	Approx. total % ash	Remarks	Insoluble in acids	Soluble in acids
Clitandra vine (c. elastica)	3.00	71	Chiefly potassium chloride, with some sodium, magnesium and sulfate.	..	..
Landolphia root (probably L. thollonii)	1.77	4	Sulfates; no chlorides	75% siliceous material	3.9% ferric oxide; 6.3% alumina and titanium oxide; 6.2% lime; 0.6% magnesia; 1.4% phosphoric anhydride
Cryptostegia sp. (1) Dried latex, cf. in Table I, before water-extraction	3.72	77	Chiefly chloride of potassium and sodium	2% siliceous material	Contained much magnesium and phosphate, some calcium and a little iron
(2) After water extraction Kok-saghyz	0.6	..	..	31% siliceous material	Contained iron, aluminum, calcium, magnesium phosphate
(1) Fermentation process	2.95	A few %	Mainly sulfates.	About 74% siliceous material	Contained iron, aluminum, phosphate as (1) but less calcium and magnesium
(2) Caustic soda process	3.00	A few %	Mainly sulfates.	About 59% siliceous material	

Only in the case of Funtumia rubber is the percentage present sufficiently high to raise the query as to whether compounders should adjust the proportion of extender in their mixes when using this rubber.

#### NITROGEN

The nitrogen content of Funtumia rubber is generally from 1 to 2 per cent, and of Ceara about 0.8 per cent, although in both cases low values are sometimes found. Landolphia rubbers invariably have a low nitrogen content; in vine rubber it is about 0.2 per cent, and in root rubber about 0.10 to 0.15 per cent.

Nitrogen is about 1 per cent in *Cryptostegia* and about 0.5 per cent in *Kok-saghyz* and *Krim-saghyz* rubbers.

#### ASH

Ash naturally varies very much with the method of preparation and the care taken, but is always much higher than in smoked sheet. Values have been found for Funtumia rubber which range from 0.2 to 1 per cent, but Landolphia vine and root rubbers are often much higher, owing to the inclusion of finely-divided bark and soil. All *Kok-saghyz* rubber so far examined has given over 2 per cent of ash.

Table IV shows the results of some qualitative or roughly quantitative analyses of ash from different types of rubber.

#### MATERIAL SOLUBLE IN NITROBENZENE

Column 7 of Table I shows that wild rubbers generally, and even clean but rather mouldy Funtumia smoked sheet, contain up to 10 per cent of very finely-divided nonrubber impurities. With the exception of the material from *Kok-saghyz* rubber, nearly all passed through a 200-mesh sieve. These impurities are separated as a dark brown powder which may contain appreciable proportions of nitrogen and mineral substances, particularly in the case of Funtumia and Ceara rubbers (Table II).

#### COPPER AND MANGANESE

No evidence has so far been obtained that wild rubbers contain excessive amounts of copper or manganese. The values are usually slightly higher than those customary for plantation Hevea.

Of the samples discussed in the tables, data are available for Hevea and Landolphia root rubber only. These were:

Hevea . . . . .	0.0008 per cent Cu.
	0.0002 per cent Mn.
Landolphia root rubber . . . . .	0.0018 per cent Cu.
	0.0008 per cent Mn.

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